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ANETHOL AND ITS ISOMERS.

[SECOND PAPER.[1]]

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ANETHOL.

I. Physical Properties.

The anethol used in this work was a product of exceptional purity[2]. It melted at 19°–21°.5 C., and distilled completely between the temperatures 231°.5 and 232°.5 C. (uncorr.). A sample portion distilled completely with steam, leaving no residue. A still purer product was obtained by recrystallization of the commercial anethol from ordinary alcohol (93.7 per cent). After recrystallization the product melted at 22°.5 C., and this melting-point remained unchanged after further recrystallization from this or other solvents. The boiling-point of this purest product was taken, using a standard thermometer, the mercury column of which was entirely surrounded with the vapor of the boiling liquid, and found to be 233°.6 C. at 731 mm. barometric pressure.[3]

[1] See This JOURNAL, **19**, 845, for the first paper on this subject.

[2] This anethol was purchased from Fritzsche Bros., of N. Y. City, a branch of Schimmel & Co., of Leipsic.

[3] This thermometer registered 0°.1 too high at this temperature according to the Prüfungs-Bescheinigung of the Physikalisch Technische Reichsanstalt, Abtheilung II, Charlottenburg, Germany. The correct boiling-point is therefore 233°.5 C.

The pure product still possessed a slight anise odor, but this was not nearly so pronounced as in the commercial product. It is soluble in all proportions in chloroform, ether, acetic ether, acetone, benzene, absolute alcohol, carbon disulphide, aniline, and petroleum ether. It is less soluble in ordinary alcohol (93.7 per cent), and may be crystallized from this solvent by cooling the solution down to 0° C. In water it is very slightly soluble, but sufficiently to impart its characteristic taste and odor to this liquid. From petroleum ether it may be crystallized by cooling the solution sufficiently.

The freezing-point of the commercial anethol, using the Beckmann freezing-point apparatus, was found to be 20°.55 C. as the mean of three very careful observations. When recrystallized from alcohol twice the purified product solidified at 21°.4 C., and further recrystallization from alcohol or from petroleum ether did not change this freezing-point. Hence the product must be regarded as pure.

The statement is made by Grimaux[1] that when heated to 100° C. for some time, the melting-point of anethol is lowered in consequence of the formation of polymers. In repeating this work it was found that, after heating anethol for nine hours on the water-bath, its melting-point was lowered about 5°. Further heating at its boiling-point (230° C.) for three hours lowered the melting-point about 1° more, and the product now left an appreciable residue when distilled in steam. This residue was a dark-colored, thick, viscous oil, heavier than water, and appeared to be identical with the product called isoanethol, obtained by Kraut and Schlun[2] by heating fluid metanethol in sealed tubes at 330° C. for several hours. In purifying anethol by distillation it is therefore better to distil in steam or under reduced pressure in order to avoid this polymerization as much as possible. The method of purification by crystallization is of course not open to this objection and is to be preferred to all others.

From alcohol anethol crystallizes in extremely thin, rectangular plates, which show parallel extinction and a biaxial optical interference figure in converged polarized light. The

[1] Bull. Soc. Chim. (Paris), (III), **15**, 778.
[2] Arch. d. Pharm. (2), **116**, 241.

acute bisectrix is apparently at right angles to the flat plates; hence the symmetry is most probably orthorhombic, though possibly monoclinic.

II. Chemical Conduct.

A. The Action of Iodine on Anethol.—A concentrated solution of iodine in acetone or potassium iodide acts at once on anethol, with evolution of heat, converting it into its polymer anisoin. Iodine alone effects this change on standing with anethol for a long time, or immediately, if the two are heated together. On the other hand, a concentrated alcoholic solution of iodine has no polymerizing action on anethol.

B. The Action of Hydrochloric Acid on Anethol. Anethol Hydrochloride.—The method employed in the preparation of this compound was slightly different from the one used by Saussure[1] and Cahours[2] in the respect that, instead of subjecting the solid anethol to the action of the gas, the latter was conducted into the melted substance, care being taken to maintain as low a temperature as possible and still keep the anethol in fluid condition. The anethol was first weighed, then hydrochloric acid gas passed in until the weight no longer increased. The reaction-product was a thick oil and had a reddish or greenish tinge when first prepared.

The amount of hydrochloric acid that anethol can absorb was determined in a few cases, as follows:

10 grams anethol absorbed 3 grams of dry hydrochloric acid gas. (Theory requires 2.5 grams for the compound,

$$C_6H_4\begin{cases}OCH_3\,(p)\\ CH_2CHClCH_3\end{cases}.)$$

30 grams anethol absorbed 8.5 grams HCl. (Theory 7.5 grams.)

14.26 grams anethol absorbed 3.43 grams HCl. (Theory 3.52 grams.)

In the last determination the weighings were carefully made

[1] Ann. chim. phys. (1), **13**, 282 (1820).
[2] *Ibid.* (III), **2**, 279 (1841).

and the results are correspondingly accurate. The other determinations were merely approximate.

Grimaux[1] states that the quantity of hydrochloric acid absorbed by anethol does not appear to be definite since he found it to vary by as much as 2 per cent in different experiments. He considers that the action is not an additive but a polymerizing one, the anethol being changed to isoanethol which holds in solution a variable amount of hydrochloric acid. The results of our work, however, do not bear out this supposition. On the contrary, they agree with the results obtained by Saussure and Cahours, both of whom found that anethol absorbed exactly the amount of hydrochloric acid required by theory for the formation of a compound of the formula, $C_{10}H_{13}O.HCl$.

The anethol hydrochloride is very unstable, and gives off hydrochloric acid fumes constantly on standing at ordinary temperatures, the decomposition being apparently the same as that which takes place on distillation ; namely, the splitting off of hydrochloric acid and formation of isoanethol. Apparently this decomposition takes place to a slight extent even during the preparation of the anethol hydrochloride. If it is allowed to go too far anomalous analytical results are to be expected.

When anethol hydrochloride is treated with alcoholic caustic potash several products result. Besides isoanethol and solid metanethol a light oil is formed which distils with steam and has a pleasant mint-like odor. This is an alcohol addition-product of anethol and will be described in another part of this paper.

C. The Action of Picric Acid on Anethol.—The picrate of anethol has been described by Ampola[2] as a solid crystallizing from alcohol in carmine-red needles melting at 60° C.

In order to compare closely the conduct of anethol with that of fluid metanethol the action of picric acid on both these compounds was investigated.

The picrate of anethol was easily formed by adding the calculated amount of picric acid to a solution of anethol in alco-

[1] Bull. Soc. Chim. (Paris), (III), **15**, (1896) 778.
[2] Gazz. chim. ital., **24** (1894), 432.

hol. The picrate could then be precipitated out with water or crystallized out by evaporation of the alcohol. The pure substance melted with decomposition at about 70° C. On standing in the air it gradually breaks down into anethol, which volatilizes, and picric acid. Alcoholic caustic potash decomposes it immediately into anethol and potassium picrate.

D. The Action of Bromine on Anethol. Anethol Dibromide.—This compound was prepared by Ladenburg's method.[1] It decomposes so readily that its crystallographic constants could not be determined. The melting-point of the pure crystals was determined as 63°–64° C. (according to Ladenburg 65° C.), but as the substance decomposes at its melting-point or even at a still lower temperature, an accurate determination could not be made.

Monobromanethol Dibromide.—Following the directions of Hell and Gärttner,[2] this compound was prepared by adding gradually to a cold ethereal solution of anethol slightly more than 2 molecules of bromine. The first half of the bromine should be added gradually, as the reaction is violent, until all the anethol is converted into the dibromide. The remainder of the bromine can then be added all at once, as the substituting action is slow. The ethereal solution, if left to evaporate spontaneously, will then deposit the crystalline monobromanethol dibromide.

Hell and Gärttner purified this product by repeated crystallization from petroleum ether, but this method is slow and unsatisfactory, since, in the first place, the compound does not dissolve easily in petroleum ether, and, in the second place, it requires a number of recrystallizations to remove the impurities. It was found, however, that the compound could be easily and quickly purified by dissolving it in a small amount of chloroform and then adding alcohol to this solution until precipitation began. The monobrom dibromide is then deposited in the form of slender prisms, which melt sharply at 102° C., the melting-point being unchanged by recrystallization from chloroform-alcohol or from ether. When heated

[1] Ann. Chem. (Liebig), Suppl. Bd. **8**, 87 (1872).
[2] J. prakt. Chem., **51** (1895) 424; see also *Ibid.*, **52**, 193 (1895).

rapidly the melting-point is somewhat higher than the one just given.

The same monobrom dibromide results, either by shaking anethol with bromine water until no more bromine is absorbed and then treating the resulting dibromide in ethereal solution with another molecule of bromine; or, by adding the calculated amount of bromine directly to anethol.

Monobromanethol dibromide is slowly decomposed if its solution in acetone, ether, chloroform, or chloroform-alcohol is kept warm for any length of time. It was therefore difficult to obtain very good crystals, although it is a substance that would otherwise crystallize unusually well. The best crystals were obtained by allowing the chloroform-alcohol solution to cool somewhat slowly.

The crystals are doubly refracting. They show the biaxial optical interference figure in converged polarized light, but in no case parallel extinction. The optical properties as well as the form of the crystals show them to belong to the triclinic system.

The four angles in one crystal zone were measured in order to compare them with the same angles on the crystals of the corresponding fluid metanethol compound. For the obtuse angles the best measurements were: 97°43′, 97°42′, 97°48′, and 97°44′; for the acute angles: 82°22′ and 82°14′. Average 97°44′ and 82°18′.

E. The Action of Nitrogen Trioxide on Anethol.—The nitrosite and its anhydride were prepared by the method of Tönnies[1] for the purpose of comparing their properties with those of the analogous fluid metanethol derivatives. The following method of preparation was finally adopted.

The theoretical amount of sodium nitrite, dissolved in water, was added to a solution of anethol in three times its volume of glacial acetic acid. The mass immediately became viscous and turbid, but it was only after standing several hours that it became nearly solid from the formation of crystalline material. It was then filtered and the contents of the filter recrystallized from ether. Crystals separated from this solvent in the form of long, slender prisms showing very clear

[1] Ber. d. chem. Ges., **11**, 1511 (1878).

faces and melting at 98° C. This compound is the anethol nitrosite anhydride or, as Boeris[1] calls it, diisonitrosoanethoil peroxide.

The nitrosite itself was obtained in small quantity by allowing the sodium nitrite and alcohol solution to react together for a much shorter time—about one-half hour—and treating the resulting viscous mass with ether. A portion of the mass dissolves in the ether and another part is deposited in fine needles which melt at about 130° C., and agree in properties with the anethol nitrosite described by Tönnies.

An attempt to prepare the glycol, $C_6H_4\begin{matrix}OCH_3\\ \diagup\\ —CH(OH)\end{matrix}\begin{matrix}CH_3\\ \diagup\\ CH(OH)\end{matrix}$, from this compound, following as closely as possible the directions of Tönnies, proved unsuccessful. Attempts to make it by Wagner's[2] method, by the oxidation of anethol with a 1 per cent solution of potassium permanganate, were equally unsuccessful.

The anhydride of the nitrosite crystallized exceedingly well and appeared to be perfectly stable at ordinary temperatures.

A microscopical examination showed the crystals to be doubly refracting and biaxial, and to contain a single plane of symmetry perpendicular to a binary axis of symmetry. They are consequently monoclinic holohedral. A large number of measurements of the six angles in the orthopinacoid zone gave closely agreeing numbers. The average measurements for the angles were: 98°46′, 33°10′.5, and 48°2′, respectively.

F. The Action of Nitrosyl Chloride on Anethol.[3]—The nitrosochloride was prepared in several different ways, all of them based on the use of nascent nitrosyl chloride. The best results were obtained by passing hydrochloric acid gas into an ethereal solution of anethol and amyl nitrite, as follows:

A slow current of dry hydrochloric acid gas was conducted into a mixture of 10 grams anethol and 8 grams amyl nitrite dissolved in 30 grams of ether. Each bubble of hydrochloric acid gas produced a transient brown color. In a few minutes

[1] Gazz. chim. ital., **21**, 183 (1891).

[2] Ber. d. chem. Ges., **24**, 3488 (1891).

[3] Tönnies: Ber. d. chem. Ges., **12**, 169 (1879); Tilden and Forster: J. Chem. Soc., **65**, 330 (1894).

the mixture became nearly solid with the nitrosochloride crystals. These were then filtered off and hydrochloric acid gas again passed into the mother-liquor until it once more became nearly solid with crystals. After this operation had been repeated three or four times the addition of hydrochloric acid gas to the mother-liquor no longer produced a precipitate, but still more of the nitrosochloride separated from the mother-liquor on the addition of alcohol. Finally, the addition of water to the remaining liquid precipitated a small amount of oily matter. The total yield of anethol nitrosochloride obtained by this method was somewhat more than 50 per cent of the theoretical amount. The product was very nearly pure when first prepared, and it is probable that a much larger yield could have been obtained by this method by careful manipulation and the use of pure amyl nitrite instead of the commercial product.

The pure nitrosochloride, when heated slowly, melts with violent decomposition at 123° C. Tilden and Forster give its melting-point as 127° C. It dissolves easily in chloroform, is moderately soluble in toluene, benzene, and acetic ether, slightly soluble in hot absolute alcohol and acetone; and almost insoluble in ordinary alcohol, ether, carbon disulphide, and petroleum ether. It decomposes when heated in solution in chloroform, toluene, acetone, or glacial acetic acid.

The crystals separate from chloroform in the form of tabular plates. An examination of their optical properties showed them to be biaxial, and to give oblique extinction whether examined perpendicularly to their broad surfaces or in cross section. They are therefore triclinic.

FLUID METANETHOL.

The preparation of this compound was carried out in the usual way; namely, by distillation of anisoin and careful separation of the resulting products. For this purpose only pure anisoin, precipitated carefully from acetone solution by alcohol, was used.

The distillation-products of the anisoin were separated by fractional distillation into three distinct compounds. One, of boiling-point 175° C., has been identified as the methyl ether

of paracresol, $C_6H_4\begin{cases}OCH_3\\CH_3(p)\end{cases}$; the second, which boils at 228°–232° C., is fluid metanethol; and the third, whose boiling-point is above 360° C., is the substance known as isoanethol.

The purification of the fluid metanethol was a tedious process. It underwent slight change when distilled under atmospheric pressure so that only an approximate degree of purity could be attained by this means. By distillation under diminished pressure (40 mm.), the purification was carried much farther, although even then slight change appeared to take place, and it was only after seven complete fractionations that a product of sharp boiling-point (142°–143° C. under 40 mm. pressure), and freezing-point (10°.4–10°.7 C.), was isolated.

This compound was finally obtained completely pure by repeated crystallization from alcohol. After one crystallization its melting-point rose to 18°–19° C. Recrystallized once more it became 22°.5 C., and after another recrystallization it still melted at 22°.5 C. This then is the melting-point of pure fluid metanethol, and it is exactly the same as the melting-point of pure anethol. The odor and taste also of this product could not be distinguished from the odor and taste of pure anethol, and its boiling-point was found to be the same as that of pure anethol.

The crystals of the fluid metanethol from alcohol could, in no way, be distinguished from the crystals of anethol from the same solvent. They formed very thin, nearly square, rectangular plates, showing the same biaxial interference figure and probable orthorhombic symmetry as the anethol crystals.

Towards chemical reagents the fluid metanethol was found to behave in every instance in exactly the same way as anethol, as the following experiments show:

A. The action of iodine in concentrated solution in aqueous potassium iodide on fluid metanethol gave a brown, tarry mass, which dissolved easily in acetone and was precipitated from this solvent, by the addition of alcohol, as a white, amorphous powder, having the same appearance and properties as anisoin.

B. A current of dry hydrochloric acid gas passed into fluid metanethol changed it into a heavier oil which could not be distinguished from a specimen of anethol hydrochloride prepared at the same time. Ten grams of the fluid metanethol absorbed 2.5 grams of dry hydrochloric acid gas—2.47 grams being the theoretical amount required for the formation of fluid metanethol hydrochloride, $C_{10}H_{12}O.HCl$. On treating this hydrochloride with alcoholic caustic potash and distilling the resulting product with steam, a light oil passed over. This had a peculiar mint-like odor and yielded anethol on distillation. The oil which resulted by similar treatment of anethol hydrochloride had these same properties and was identified as the alcohol addition-product of anethol,

$$C_{10}H_{12}O.C_2H_5OH.$$

C. The addition of picric acid to an alcoholic solution of fluid metanethol immediately caused the solution to turn red, owing to the formation of the picrate. On evaporation, or by addition of water to the solution, the picrate separates out in the form of bright-red needles, which melt approximately at 70° C. The compound decomposes at its melting-point and is identical in appearance and properties with the corresponding anethol compound.

D. Dibromide of fluid metanethol: This compound was prepared in the same way as the anethol dibromide: that is, by adding bromine, drop by drop, from a burette to a cooled solution of fluid metanethol in ether, until a drop imparted its color to the whole solution. The excess of bromine was removed by shaking the mixture with water saturated with sulphur dioxide. The washed ethereal solution then left behind on evaporation a mass of needle-shaped crystals, which were easily obtained pure by recrystallization from petroleum ether. Their melting-point was determined at 63°.5 C. This compound could, in no way, be distinguished from anethol dibromide.

Monobromine derivative of the dibromide of fluid metanethol: This compound was prepared in exactly the same way as the corresponding anethol compouud. The melting-point of the pure product was determined as 102° C. As to its

crystal appearance, solubility, and stability, it is only necessary to repeat what has been said in this connection about the corresponding anethol compound. A microscopical examination showed the crystals to belong to the triclinic system. The same angles were measured as in the case of the monobromanethol dibromide and the following results obtained: Average for the obtuse angles 97° 56′; for the acute angles 82° 6′.

E. The nitrosite and nitrosite anhydride of fluid metanethol, prepared in the same way as the anethol compounds, did not differ from them in any way so far as could be detected. Only a small amount of the nitrosite was obtained, but enough to determine its melting-point, which was found to be 125°–130° C. The anhydride was formed in larger quantity and was more carefully examined. The following characteristics were determined: The compound crystallizes in long, slender, slightly yellow crystals which melt at 98° C. Crystallographically they differ in no respect from the crystals of anethol nitrosite anhydride. The angles in the orthopinacoid zone of a number of crystals were measured, the average angles being found to be 98°46′.5, 33°11′, and 48°2′, respectively.

F. The action of nascent nitrosyl chloride on fluid metanethol produces a compound of the same appearance, melting-point, solubility, and stability as the nitrosochloride of anethol. The symmetry and optical properties of the crystals were determined and the same results obtained as in the case of the anethol compound.

By a comparison of the entire conduct of fluid metanethol with that of anethol it will be seen that it is the same substance. There is therefore no longer any need of the name fluid metanethol to designate the chief product of the distillation of anisoin, as it is, in reality, anethol.

A few other investigations will now be described, first considering the action of alcoholic caustic potash on anethol hydrochloride.

The Alcohol Addition-product of Anethol, $C_{10}H_{12}O.C_2H_5OH$.

The addition of a slight excess of alcoholic caustic potash

to anethol hydrochloride at first produced no visible effect, but the mixture soon began to get warm and deposited a copious precipitate of potassium chloride. The mixture was then washed with water, to remove the alcohol and inorganic compounds, and distilled with steam.

Two products were obtained by this treatment in about equal quantities. One, an oil resembling anethol, passed over with the steam. The other remained in the distilling-flask as a semi-solid mass, heavier than water, and was found to consist chiefly of isoanethol and solid metanethol.

The part of the mixture that passed over with the steam was a thin, colorless oil, lighter than water, and had a strong, pleasant, mint-like odor, entirely different from that of anethol. The following experiments showed this substance to be an alcohol addition-product of anethol of the formula

$$C_{10}H_{12}O.C_2H_5OH.$$

(1) The purest product, in ether solution, would take up only one-twelfth the amount of bromine that the same weight of anethol would absorb. It is consequently saturated, there being no doubt that, when entirely free from anethol, it would not absorb bromine at all.

(2) When heated no change is visible until the temperature reaches 200°–210° C. Bubbles then begin to rise from the bottom of the flask and, as the temperature is further increased, the liquid boils vigorously. On distillation, 13 grams of the compound yielded the following products:

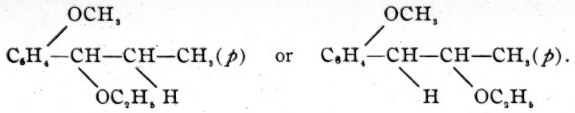
(*a*) 2.5 grams of a liquid having the odor and boiling-point of alcohol, and yielding iodoform when treated with potassium hydroxide and iodine. This liquid is evidently alcohol.

(*b*) Approximately 9 grams of a liquid boiling at 225°–230°. This solidified in a freezing-mixture of hydrochloric acid and ice and, by its odor, melting-point, and boiling-point, was identified as anethol.

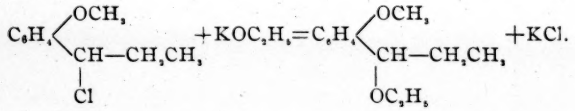
(*c*) There still remained in the distilling-flask about 2 grams of a reddish liquid from which crystals of solid metanethol separated on cooling.

The relative quantities of anethol and alcohol obtained in this experiment indicate that they were present molecule for

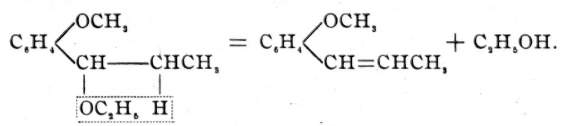
molecule in the original compound, to which we must accordingly assign the formula $C_{10}H_{12}O.C_2H_5OH$. Structurally it should probably be represented by one of the two following formulas :



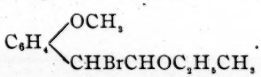
This alcohol addition-product of anethol probably results from the anethol hydrochloride in accordance with the following equation :



The decomposition of the product on heating would be represented as follows :



Perhaps the product obtained by Hell and von Gunthert[1] by the prolonged action of boiling alcohol on anethol dibromide has an analogous constitution. This compound, from the percentage of bromine it contained, was judged to have the formula $C_{10}H_{12}BrO.C_2H_5OH$, and might be regarded as the alcohol addition-product of bromanethol,



The alcohol addition-product of anethol is but slightly decomposed when distilled with steam. When distilled directly under diminished pressure (40 mm.) the decomposition is greater, but still the larger part remains unaltered.

[1] J. prakt. Chem., **52**, 199 (1895).

Anethol Hydrobromide.

The hydrobromide of anethol is not mentioned in the literature. It is formed by the action of dry hydrobromic acid gas on anethol in the same way that anethol hydrochloride is formed by the action of dry hydrochloric acid.

A current of dry hydrobromic acid gas was passed into 20 grams of liquid anethol until further addition no longer increased the weight. It was found that 12.5 grams of hydrobromic acid had then been absorbed. In order to remove any excess of hydrobromic acid air was then passed through the liquid until the fumes of the acid, which were copiously evolved at first, ceased to be given off, and even its odor could not be detected. By this treatment with air the product lost 1.5 grams in weight, hence there remained 11 grams of hydrobromic acid in combination with the anethol. The calculated amount with which 20 grams of anethol should unite to form the hydrobromide, $C_{10}H_{12}O.HBr$, is 10.95 grams; and, as succeeding experiments confirmed these results, there can be but little doubt that this formula correctly represents the compound formed in this reaction.

The freshly prepared, crude hydrobromide was tinged slightly green, but became colorless when washed with water. It had previously been noticed that anethol hydrochloride sometimes had this same color when first prepared.

Anethol hydrobromide is a heavy oil of the same consistency and general appearance as the hydrochloride. It does not decolorize a trace of bromine and is consequently saturated. When it is decomposed with alcoholic caustic potash and the resulting oil is distilled, the products are the same as result from the distillation of anethol hydrochloride—anethol and isoanethol.

The hydrobromide reacts readily with aniline, pyridine, piperidine, or zinc dust, yielding resinous products that were not fully identified, but which consisted in part of isoanethol and solid metanethol.

The Action of Sulphuric Acid on Anethol.

Anethol itself apparently does not dissolve in sulphuric acid. Dilute sulphuric acid has no appreciable effect upon it

unless the two are left in contact for a considerable time. The concentrated acid polymerizes it at once into anisoin, and the latter dissolves slowly, yielding a red solution. Hot concentrated, or fuming, sulphuric acid acts violently on anethol, causing a rapid evolution of sulphur dioxide and completely charring the mass which is left.

It is stated by Cahours[1] that the red solution, formed by the action of sulphuric acid on anisoin, contains an acid substance which unites with baryta and lime with the formation of resinous products. These he did not further examine.

In order to determine the nature of this acid we have prepared and examined it as follows: 5 grams of anethol were treated, drop by drop, with concentrated sulphuric acid until about 20 grams of the latter had been introduced. The anisoin, which was first formed, dissolved very slowly, but at the end of two days had wholly disappeared. After standing still another day the addition of a liter of water to the red solution did not produce the least turbidity. This diluted solution was nearly neutralized with precipitated chalk, filtered, and the filtrate, after the addition of a little lime-water, evaporated to small bulk on the water-bath. The residue was a resinous mass which dried to a powder on still longer standing, the latter being extremely soluble in water, although very insoluble in alcohol, acetone, or ether. Attempts were made to crystallize it from water or a mixture of water with methyl or ethyl alcohols, but the same gummy product always separated out. It was not sufficiently soluble to crystallize from solvents containing no water, and, when any water was present, enough would be taken up by the substance to form a resinous mass.

The substance was finally dissolved in alcohol (50 per cent) and reprecipitated by the addition of alcohol (90 per cent). The white powder thus obtained was subjected to the same treatment again and then dried at 120° C. until its weight was constant. An analysis of this dried product for calcium gave the following results:[2]

[1] Ann. chim. phys. (III), **2**, 274 (1841).

[2] In the calculation of all the analyses in this work the atomic weights used were: C = 12, O = 16, H = 1, S = 32, Ca = 40.

I. 0.2550 gram substance gave 0.0723 gram $CaSO_4$.
II. 0.2454 gram substance gave 0.0679 gram $CaSO_4$.

	Calculated for $(C_{10}H_{13}OSO_4)_2Ca$.	Calculated for $(C_{10}H_{11}OSO_3)_2Ca$.	Found. I.	Found. II.
Ca	7.54	8.1	8.34	8.13

Although from the method of preparation and properties of the salt it was expected that it would agree in composition with the first formula, the analyses indicate that the second formula is correct. Gerhardt[1] made an acid by the action of concentrated sulphuric acid on the so-called fluid metanethol, to which he gave the name sulphanethinic acid. From this acid he prepared the barium salt, which resembled the above calcium salt closely and on analysis gave results in accord with the formula $(C_{10}H_{11}OSO_3)_2Ba + 2H_2O$.

Anethol Dihydride (Parapropyl Anisol).[2]

The reduction of anethol was accomplished by adding to its solution in absolute alcohol three times the theoretical amount of sodium necessary for the formation of the dihydro addition-product. The sodium was introduced in bits the size of a pea, the whole operation taking perhaps two hours. The yield of the reduction-product was found to be much larger when the reaction took place at as low a temperature as possible than when it took place at the boiling temperature of the alcohol. Under the former conditions a 50 per cent yield was obtained.

The addition of water to the reaction-products precipitated an oil which, after being washed, dried, and fractionally distilled, was found to contain, besides anethol, a liquid which boiled at 210°–214° C. This would unite directly with only about 0.1 the amount of bromine that would be absorbed by the same weight of anethol. It was evident from this conduct that the reduction-product was a saturated compound but still containing as an impurity a small quantity of anethol. This remaining trace was completely removed by dissolving the mixture in a concentrated solution of iodine in acetone and heating to boiling for a few minutes. Alcohol was then

[1] J. prakt. Chem., **36**, 275 (1845).

[2] See also Ladenburg: Ann. Chem. (Liebig), Supl. Bd. **8**, 89 (1872); Landolph: Ber. d. chem. Ges., **13**, 144 (1880); and Klages: *Ibid.*, **32**, 1436 (1899).

added to precipitate the anisoin, the mixture boiled with zinc dust to remove the iodine, and filtered. Water added to the filtrate precipitated an oil which was then further purified by being washed with water, dried, and redistilled. The distillate would not unite with bromine and was consequently free from anethol. Its boiling-point was determined as 212°.5–213°.5 C. (corr.) at 728 mm. barometric pressure. A combustion gave the following results :[1]

0.1771 gram substance gave 0.5178 gram CO_2, and 0.1538 gram H_2O.

	Calculated for $C_{10}H_{14}O$.	Found.
C	80.00	79.73
H	9.33	9.65

From its boiling-point and percentage composition we must conclude that this substance is parapropylanisol,

$$C_6H_4\begin{cases}OCH_3\\C_3H_7(p)\end{cases};$$

and, as it is formed by the reduction of anethol, it is probably the normal propyl compound. It was identical with one of the compounds formed by heating anethol under pressure.[1]

ANISOIN.

Of the methods described for the preparation of anisoin the two which have been especially recommended are : (1) The polymerization of anethol by means of concentrated sulphuric acid ; and (2) The polymerization by means of a concentrated solution of iodine in aqueous potassium iodide. There are disadvantages to both of these methods. Unless the substances are left in contact for a long time, the anisoin formed will retain included some unchanged anethol, as well as a certain quantity of the reagent, and will consequently be difficult to purify.

A method which on repeated trial in this work has been found to give much better results is the one described below. To a moderately concentrated solution of anethol in acetone,

[1] This analysis was made by Mr. J. E. Teeple, to whom we wish here to express our thanks.

[2] This JOURNAL, **19**, 863.

iodine is added until no more will dissolve. The mixture is heated to boiling for a few minutes, after which the iodine is removed by adding zinc dust, little by little, to the warm solution until it becomes nearly colorless. This solution, which must not be too concentrated, is then filtered slowly into several times its volume of alcohol. The anisoin is thus thrown down as a white powder, nearly pure.

No anisoin is formed by adding anethol to a concentrated solution of iodine in alcohol even though the mixture be heated to boiling.

Methyl Ether of Paracresol.

When anisoin is distilled there is one product formed in so small quantity that it has not hitherto been isolated. By distilling a large amount of anisoin (500 grams) and carefully fractionating the resulting products, we obtained, together with approximately 250 grams of anethol and 80 grams of isoanethol, about 20 grams of a liquid which distilled at 173°–175° C.

This liquid doubtless still contained a slight trace of anethol, but so little that it could scarcely be detected by testing an ethereal solution with bromine. One-fiftieth part of a gram of bromine imparted its color to an ethereal solution of 1 gram of the substance. Hence it follows that the substance not only does not contain anethol, but is itself a saturated compound. Combustion analyses gave the following results :[1]

I. 0.2465 gram substance gave 0.1727 gram H_2O, and 0.8084 gram CO_2.

II. 0.1986 gram substance gave 0.1475 gram H_2O, and 0.5719 gram CO_2.

	Calculated for $C_8H_{10}O$.	Found. I.	II.
C	78.68	78.38	78.54
H	8.19	7.79	8.25
O	13.13	13.83	13.21

The analyses show that the compound is correctly represented by the formula $C_8H_{10}O$.

This same compound was obtained in our previous investi-

[1] These analyses were made by Mr. J. E. Teeple, to whom we wish here to express our thanks.

gation by heating anethol under pressure, and analyses of this product and molecular weight determinations showed it to have the composition $C_8H_{10}O$.

The percentage composition of the compound, its boiling-point and its other properties, show it to be identical with the methyl ether of paracresol described in the literature. It consequently has the structural formula, $C_6H_4\begin{cases}OCH_3\\CH_3(p)\end{cases}$. It is probably formed by the action of heat on the anethol (or fluid metanethol), resulting from the decomposition of anisoin according to the following equation:

$$C_6H_4\begin{cases}OCH_3\\CH=CHCH_3\end{cases} = C_6H_4\begin{cases}OCH_3\\CH_3\end{cases} + C_2H_2.$$

SUMMARY OF RESULTS.

Anethol and Fluid Metanethol.

The properties and reactions of anethol and fluid metanethol have been given especial prominence in this work because, from the results of our earlier investigations, it seemed probable that they were stereoisomers of the maleic-fumaric acid type and would be represented by the two formulas:

I. $C_6H_4\begin{cases}OCH_3(p)\\C-H\\\|\\H-C-CH_3\end{cases}$ and II. $C_6H_4\begin{cases}OCH_3(p)\\C-H\\\|\\H_3C-C-H\end{cases}$.

It was to be expected that two stereoisomers of this type would resemble each other very closely; and that, with many reagents, they would yield exactly the same products. Consequently it was only after the two substances were very carefully examined and found to exhibit no differences whatever, either in their own conduct or in the conduct of their derivatives, that their complete identity was finally established. The facts upon which this conclusion is based may be briefly summarized as follows:

1. The physical properties of the two are identical. In

odor, taste, boiling-point, melting-point, specific gravity, and crystal form, the pure products exhibit no differences.

2. Both substances show exactly the same chemical conduct.

They yield the same dibromide and monobrom dibromide, which conduct is a strong proof of their identity since stereoisomers of the formulas given above should not yield identical derivatives of this character.

They yield the same hydrochloride, nitrosite, nitrosite anhydride, nitroso chloride, and picrate. This conduct might not preclude the possibility of their being stereoisomers, but it at least shows conclusively that they are structurally identical.

The identity in conduct of these compounds toward polymerizing and oxidizing agents might also be cited, but the evidence seems already conclusive that anethol and fluid metanethol are one and the same compound.

That the true character of fluid metanethol was not earlier discovered is doubtless due to the difficulty of separating it from the methyl ether of paracresol which is formed simultaneously with it. The presence of this impurity, even in small quantity, lowers the melting-point of anethol many degrees and completely masks its odor.

Anethol Hydrochloride.

The conclusion of Saussure and Cahours that the product formed by the action of hydrochloric acid on anethol is a chemical compound of the formula $C_{10}H_{12}O.HCl$, has been confirmed by the results obtained in this investigation. One molecule of anethol has been found to absorb exactly 1 molecule of hydrochloric acid. The resulting product will not take up bromine in the cold and hence contains no free anethol. Moreover, by the action of alcoholic caustic potash, it yields an alcohol addition-product of anethol,

$$C_{10}H_{12}O.C_2H_5OH,$$

the formation of which it is difficult to explain without assuming that the hydrochloride is first formed. Also, the fact that anethol absorbs exactly 1 molecule of hydrobromic acid,

with the formation of a saturated chemical compound, would lead us to infer by analogy that its union with hydrochloric acid is of the same character.

The Alcohol Addition-product of Anethol.

A compound of the formula $C_{10}H_{12}O.C_2H_5OH$ is formed by the action of alcoholic caustic potash on anethol hydrochloride. This compound has a pleasant mint-like odor. It is a thin liquid, lighter than water, and is but slightly decomposed when distilled with steam. When distilled alone it breaks down completely, yielding alcohol, anethol, and higher-boiling products. It is not attacked by bromine in the cold.

Anethol Hydrobromide.

Anethol rapidly absorbs hydrobromic acid gas until it has taken up the amount required for the formation of a compound of the formula $C_{10}H_{12}O.HBr$. The hydrobromide is a heavy oil closely resembling anethol hydrochloride in appearance and conduct. When decomposed by alcoholic caustic potash and distilled, it yields as the chief products anethol and isoanethol.

Parapropylanisol.

This compound results from the action of sodium on an alcoholic solution of anethol, and is also formed as one of the products when anethol is heated at a high temperature under pressure. Analyses and molecular weight determinations show its formula to be $C_{10}H_{14}O$; and, since it is formed by the addition of two hydrogen atoms to the anethol molecule, its structure is most probably represented by the formula,

$$C_6H_4\begin{cases}OCH_3\\ CH_2CH_2CH_3(p)\end{cases}.$$

Anisoin.

It has been found most practicable to prepare anisoin by adding anethol to a saturated solution of iodine in acetone and heating the resulting mixture to boiling for a few minutes. By this means the anethol appears to be rapidly and completely converted into anisoin.

When distilled, anisoin is completely decomposed, yielding the compounds anethol, isoanethol, and the methyl ether of paracresol.

Methyl Ether of Paracresol.

One of the products formed by the breaking down of anisoin on distillation is a light, colorless oil, of pungent odor, which boils at a temperature of 175° C. This same compound has been previously obtained by the action of heat and pressure on anethol. Perhaps, in its formation from anisoin, the latter is first converted into anethol, and this is then partially decomposed into the lower-boiling product. The physical properties of this compound, as well as its percentage composition and molecular weight, identify it as the methyl ether of paracresol, $C_6H_4\begin{cases}OCH_3\\CH_3(p)\end{cases}$.

CORNELL UNIVERSITY, ITHACA, N. Y.,
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THE SUPPOSED ISOMERIC POTASSIUM SODIUM SULPHITES.[1]

BY GEO. S. FRAPS.

INTRODUCTION.

The prevailing view in regard to the structure of sulphurous acid is that it is asymmetrical and has the formula H—SO_2—OH. From this formula it is theoretically possible to derive two isomeric sodium potassium sulphites; namely, K—SO_2—ONa and Na—SO_2—OK. Descriptions of these salts are on record. By neutralizing a concentrated aqueous solution of acid potassium sulphite with sodium carbonate, and precipitating with alcohol, A. Röhrig[2] obtained fine lustrous crystals of the composition $KNaSO_3 + 2H_2O$, which he believed to be isomeric with crystals of the same composition made in a similar manner from acid sodium sulphite and potassium carbonate. The statement was probably based on the assumed reactions:

[1] This work was suggested by Prof. Ira Remsen, and conducted under his direction in the laboratory of the Johns Hopkins University.

[2] J. prakt. Chem. [2], **37**, 250.

$2H—SO_2—OK + Na_2CO_3 = 2Na—SO_2—OK + CO_2 + H_2O$;
$2H—SO_2—ONa + K_2CO_3 = 2K—SO_2—ONa + CO_2 + H_2O$.

H. Schwicker[1] prepared the salts in a similar manner, but, instead of precipitating with alcohol, he evaporated the solutions in a desiccator over sulphuric acid. The crystals contained different amounts of water of crystallization. The one from acid potassium sulphite and sodium carbonate separated in crystals having the composition $NaKSO_3 + 2H_2O$; the crystals of the other, from acid sodium sulphite and potassium carbonate, had the formula $NaKSO_3 + H_2O$.

By the aid of the reaction between ethyl iodide and a sulphite, in which the metal united to the sulphur is replaced by ethyl, thus:

$$C_2H_5I + Na—SO_2—ONa = C_2H_5—SO_2—ONa + NaI,$$

we might be able to determine if the salts described above are isomeric or identical, since, if different, the one should yield a sodium ethylsulphonate, the other a potassium ethylsulphonate:

$$C_2H_5I + K—SO_2—ONa = C_2H_5—SO_2—ONa + KI;$$
$$C_2H_5I + Na—SO_2—OK = C_2H_5—SO_2—OK + NaI;$$

or more correctly, the double salt $4C_2H_5SO_3Na + KI$ could be extracted from the reaction-product of the first, and the salt $4C_2H_5SO_3K + NaI$ from that of the other.

According to Schwicker, when the sodium potassium sulphite made from acid sodium sulphite and potassium carbonate is heated in aqueous solution in a sealed tube with ethyl iodide and the product recrystallized from alcohol, it contains sodium and potassium in the ratio Na : K : : 4 : 1, corresponding to the double salt $4C_2H_5SO_3Na + KI$. The salt from acid potassium sulphite and sodium carbonate under the same conditions yielded a product containing Na : K : : 1 : 4, corresponding to the double salt $4C_2H_5SO_3K + NaI$. This indicates that isomeric salts have been prepared, having the formulas $K—SO_2—ONa$ and $Na—SO_2—OK$. Schwicker states further that, by boiling the isomeric sulphites with ammonium

[1] Ber. d. chem. Ges., **22**, 1728.

polysulphide, they are converted into isomeric thiosulphates, which, when heated with ethyl bromide (Bunte's reaction), yield, the one the sodium salt, $C_2H_5S_2O_3Na + H_2O$, the other the potassium salt, $C_2H_5S_2O_3K$.

More recently this work has been repeated by K. Barth[1] in the course of an investigation on the complex salts of sulphurous acid. The acid sulphite was formed by passing sulphur dioxide into a strong solution of sodium (or potassium) hydroxide, and neutralized by the requisite quantity of a solution of potassium (or sodium) hydroxide. Alcohol precipitated both salts as water-free crystals, not the crystals

$$NaKSO_3 + 2H_2O,$$

of Röhrig. Under ordinary conditions, the crystals formed by evaporation over sulphuric acid in a desiccator were water-free, but, when cooled, crystals separated which had the composition of those obtained by Schwicker.

Barth heated the equally concentrated solutions of the water-free salts—the concentration is not given—with ethyl iodide in a sealed tube at 130° for three hours, evaporated to dryness, extracted the residue with 97 per cent alcohol, and recrystallized from 99 per cent alcohol. The product was analyzed by igniting with sulphuric acid, and determining the sulphuric acid in the residue, from which the ratio Na : K was calculated. The potassium sodium sulphite from acid sodium sulphite and caustic potash yielded a product containing Na : K : : 1 : 1.3 (mean of two preparations) ; theory requires for the salt $4C_2H_5SO_3Na + KI$, Na : K : : 4 : 1. The salt from acid potassium sulphite and sodium hydroxide yielded a product containing Na : K : : 1 : 2.9 (mean of two) instead of Na : K : : 1 : 4 as required by the theory. The two sodium potassium sulphites yielded different products, and must therefore be different.

Barth explained the deviation of the results from the theoretical in terms of the theory of electrolytic dissociation. He showed that the salts dissociate into three ions. When the ions K, Na, SO_3, from the salt KSO_3ONa, for example, are caused to reunite, as by evaporation of the solution, or precipitation

[1] Ztschr. phys. Chem., 9, 77.

with alcohol, there is no reason to suppose the salt KSO_2ONa to be formed again, but rather a mixture of the salts $NaSO_2OK$, KSO_2ONa, Na_2SO_3, and K_2SO_3, and the pure salt KSO_2ONa could not be obtained. Again, when the reaction betweed the ethyl iodide and the salt has taken place, the potassium iodide and the sodium ethylsulphonate must be dissociated to some extent, and potassium ethylsulphonate and sodium iodide must be formed when the solution is evaporated to dryness. The alcohol from which the salt is recrystallized must exert some influence on its composition also. Hence one could not expect the ratio of sodium to potassium to agree with that required by theory. Barth states that "an infallible conclusion as to the different constitution of the sulphites cannot be drawn from the results obtained, but only that in one solution more molecules of KSO_2ONa were present, in the other more molecules of $NaSO_2OK$, and hence the probability of the isomerism of the solid bodies."

The conclusion does not appear to be accepted. Hantzsch[1] asserts that structural isomerism is unknown among inorganic compounds. A Sabanejeff[2] observes that the isomerism of the potassium sodium sulphites can by no means be regarded as proved.

The stability of the salts appears incompatible with the theory of electrolytic dissociation, since they dissociate into three ions. If dissociation is conceived as a dynamic condition, in which the molecules are in a constant vibration of decomposition and recombination, it is difficult to see how the salts $K—SO_2—ONa$ and $Na-SO_2—OK$, supposing them to exist as solids, could long retain their individuality even in concentrated solutions. In a certain time the undissociated portion of the salts must assume a condition of equilibrium of the salts K_2SO_3, Na_2SO_3, $KNaSO_3$, which would be the same whether sodium potassium sulphite or potassium sodium sulphite were the starting-point. That is to say, isomeric salts of such a nature could not remain different in aqueous solution, even if they exist in the solid state.

[1] Ann. Chem. (Liebig), **292**, 342; **296**, 100, 111.
[2] Ztschr. anorg. Chem., **17**, 481.

The same objection applies to the reaction used to prove that the two salts are different, or Guldberg and Waage's law of mass action may be applied. Supposing the following reactions to take place :

$$C_2H_5I + KSO_2ONa = C_2H_5SO_2ONa + KI;$$
$$C_2H_5I + NaSO_2OK = C_2H_5SO_2OK + NaI.$$

The reaction

$$C_2H_5SO_2ONa + KI \rightleftarrows C_2H_5SO_2OK + NaI$$

must surely be a reversible one, and the condition of equilibrium would be the same from either starting-point; at 130° the adjustment would not take long.

These considerations throw doubt upon the work before cited, and it was repeated. Before going into details, a brief summary of the experiments will be given. Four sets of the double salts were prepared, under conditions judged most favorable to the appearance of isomerism, one member of the set from acid sodium sulphite and potassium carbonate or hydroxide, the other from acid potassium sulphite and sodium carbonate or hydroxide. The salts in each set were made under exactly similar conditions and at the same time, with the exception of set I, as hereafter noted. In set I the salts were not analyzed; in set II they were slightly different in composition; and in sets III and IV they had practically the same composition.

The two salts, which it was thought might be isomeric, were heated with ethyl iodide, the products extracted with alcohol and analyzed, the supposed isomers being subjected to conditions as nearly identical as possible. Seven experiments were thus made, in which the strength of alcohol, time of heating, etc., were varied slightly. If the salts were isomers, analysis should show a difference in the ratio of sodium to potassium; in none of the experiments was there any decided variation. It is believed that the conditions were as favorable for the isomerism to reveal itself as it was possible to make them. The writer therefore feels justified in making the statement that we have no evidence that isomeric potassium sodium sulphites exist.

The table shows the ratio of sodium to potassium as found by analysis of the double sulphonate prepared from the two salts.

	$NaSO_3OK$.	KSO_3ONa.
Na : K required by theory....	1 : 4	4 : 1
" found by Barth	1 : 2.9	1 : 1.3
" Experiment I	1 : 1.57	1 : 1.40
" " II	1 : 1.43	1 : 1.37
" " III	1 : 1.89	1 : 2.17
" " IV	1 : 1.59	1 : 1.57
" " V	1 : 2.09	1 : 2.10
" " VI	1 : 2.06	1 : 2.01
" " VII	1 : 1.82	1 : 1.73

The variation in the ratio Na : K in the different experiments is ascribed to the difference in the conditions. The stronger the alcohol used, the wider the ratio. Recrystallization from alcohol increased the ratio also, as may be seen by comparing Experiments I, II, and IV, in which the sulphonate was not recrystallized, with Experiments III, V, VI and VII, in which it was recrystallized from alcohol. The slight variation between the two members of a set was to be expected and is probably due to the alcohol.

EXPERIMENTAL.

Experiment I.—Sulphur dioxide was passed into a cooled solution of 11.5 grams of potassium carbonate in 75 cc. water until the weight gained was that required for the formation of acid potassium sulphite. Nine grams of sodium carbonate were added, air drawn through to remove carbon dioxide, and the salt precipitated with alcohol. It was not analyzed.

Ten grams of the above salt, 11 grams ethyl iodide, and 15 cc. water were heated two and a half hours in a sealed tube to 130°–140°, and the tube allowed to cool over night. The solution was evaporated to dryness, and the product extracted with laboratory alcohol. It was not recrystallized.

Analysis showed the ratio of sodium to potassium to be Na : K : : 1 : 1.57. Theory for $4C_2H_5SO_3K + NaI$, 1 : 4.

(1) 0.3381 gram substance, ignited with sulphuric acid, gave 0.1922 gram sulphates, yielding 0.2771 gram barium sulphate.

Per cent SO_3 in sulphates = 49.52. Na : K : : 1 : 1.54.

(2) 0.2848 gram substance gave 0.1612 gram sulphates, yielding 0.2320 gram barium sulphate.

Per cent SO_3 in sulphates = 49.43. Na : K : : 1 : 1.59.

Proceeding exactly as above, and performing the operations at the same time and under the same conditions, but using a solution of 9 grams sodium carbonate in 32 cc. of water, and adding 11.5 grams of potassium carbonate, the supposed isomeric salt was prepared. It was treated with ethyl iodide under the same conditions, at the same time as the above, the product extracted with the same alcohol, and analyzed. The ratio of sodium to potassium was 1 : 1.40; a slight difference, but no evidence of isomerism.

(1) 0.3892 gram substance gave 0.2117 gram sulphates, yielding 0.3067 gram barium sulphate.

Per cent SO_3 in sulphate = 49.77 Na : K : : 1 : 1.38.

(2) 0.2858 gram substance gave 0.1545 gram sulphates, yielding 0.2235 gram barium sulphate.

Per cent SO_3 in sulphates = 49.69. Na : K : : 1 : 1.41.

In the experiment above described, the two salts were prepared in solution of different concentrations, for the reason that it seemed to be desirable to use as concentrated solutions as possible, and acid potassium sulphite is less soluble than acid sodium sulphite. In succeeding experiments the salts are prepared in solutions of equivalent concentration.

Experiment II.—The salts were prepared as in Experiment I, with the exception that the solutions were of different concentration, *i. e.*, 23 grams of potassium carbonate in 120 cc. water, and 18 grams of sodium carbonate in the same quantity.

Analysis of the salts :

(*a*) Salt from acid potassium sulphite and sodium carbonate :

(1) 0.3344 gram substance, with sulphuric acid, gave 0.3657 gram mixed sulphates, which yielded 0.5403 gram barium sulphate. Na : K : : 1 : 0.94.

(2) 0.2899 gram substance gave 0.3180 gram sulphates, yielding 0.5403 gram barium sulphate. Na : K : : 1 : 0.99.

(*b*) Salt from acid sodium sulphite and potassium carbonate:

(1) 0.4505 gram substance gave 0.4756 gram sulphates, yielding 0.7119 gram barium sulphate. Na : K : : 1 : 0.72.

(2) 0.5432 gram substance gave 0.5762 gram sulphates, yielding 0.8614 gram barium sulphate. Na : K : : 1 : 0.74.

The ratio of sodium to potassium in the two salts is different. The analyses show the crystals to be water-free.

Ten grams of the salt (*a*), from acid potassium sulphite and sodium carbonate, 11 grams ethyl iodide, and 21 cc. water, were heated three hours in a sealed tube to 130°–140°. The solution was evaporated to dryness, the product extracted with laboratory alcohol, and analyzed. The ratio Na : K was found to be 1 : 1.43.

(1) 0.1881 gram substance, ignited with sulphuric acid, gave 0.1004 gram sulphates, which yielded 0.1452 gram barium sulphate.

Per cent SO_3 in sulphates = 49.67. Na : K : : 1 : 1.44.

(2) 0.2580 gram substance gave 0.1389 gram sulphates, yielding 0.2010 gram barium sulphate.

Per cent SO_3 in sulphates = 49.70. Na : K : : 1 : 1.41.

Ten grams of salt (*b*) was treated as above and at the same time. The ratio of Na : K in the product was 1 : 1.37. Salt (*a*) was not different from salt (*b*).

(1) 0.1500 gram substance gave 0.0798 gram sulphates, yielding 0.1162 gram barium sulphate.

Per cent SO_3 in sulphates = 50.01 Na : K : : 1 : 1.23.

(2) 0.2179 gram substance gave 0.1164 gram sulphates, yielding 0.1679 gram barium sulphate.

Per cent SO_3 in sulphates = 49.54. Na : K : : 1 : 1.51.

The composition of the two products was practically the same.

It will be noted that laboratory alcohol of unknown strength was used in the foregoing experiments. The strength of the alcohol must have some effect on the composition of the product, since that double salt would crystallize out that was most insoluble under the conditions of the experiment. For this

reason it was determined to repeat the work, using alcohol of different strength.

The double sulphites used in the experiments about to be described were prepared as follows: A solution of caustic potash was prepared, containing 172.2 grams of caustic potash in a liter, the strength being determined by titration with standard acid, and also a solution of caustic soda containing 124.2 grams per liter. 100 cc. of the solution were cooled with ice-water, and sufficient dry sulphur dioxide (from sodium sulphite and sulphuric acid) passed in to form the acid salt, controlling the amount of sulphur dioxide by weighing. In case an excess of sulphur dioxide was absorbed, the volume of the solution containing the required amount of the proper alkali was added, keeping the liquid cool. The acid sulphite so formed was neutralized with the requisite volume of the other alkali and the double salt precipitated immediately with 500 cc. of alcohol, washed with alcohol, and dried on drying-paper. It is believed that these conditions are most favorable to the production and retention of the isomerism, if it exists.

Experiments III and IV.—Salts were prepared as just described, and analyzed.

(*a*) From acid potassium sulphite and caustic soda:

(1) 0.5150 gram substance gave 0.5705 gram sulphates, and yielded 5×0.1637 gram K_2PtCl_6.

$K_2O = 30.69$ per cent. $Na : K :: 1 : 0.86$.

(2) 0.5200 gram substance gave 0.5759 gram sulphates, and 5×0.1664 gram K_2PtCl_6.

$K_2O = 30.85$. $Na : K :: 1 : 0.87$.

(*b*) Salt from acid sodium sulphite and caustic potash.

(1) 0.5409 gram substance gave 0.5956 gram sulphates, and yielded 5×0.1703 gram K_2PtCl_6.

$K_2O = 30.40$. $Na : K :: 1 : 0.85$.

(2) 0.5080 gram substance gave 0.5585 gram sulphates, and yielded 5×0.1583 gram K_2PtCl_6.

$K_2O = 30.08$. $Na : K :: 1 : 0.84$.

The salts had practically the same composition and were anhydrous.

Experiment III.—Ten grams of each of the above salts, 21 grams water, and 11 grams ethyl iodide, were heated in sealed tubes for three hours at 130°–140°. The tubes cooled over night. Their contents were then evaporated to dryness, extracted with 500 cc. of alcohol, sp. gr. 0.839, and recrystallized from 250 cc. of alcohol of sp. gr. 0.7975.

Analysis of the products.

(*a*) From salt (*a*).

(1) 0.2421 gram substance gave 0.1325 gram sulphates, and yielded 0.2546 gram K_2PtCl_6.

$$K_2O = 20.3. \quad Na : K :: 1 : 1.79.$$

(2) 0.7376 gram substance gave 0.4050 gram sulphates, and yielded $5/2 \times 0.3206$ gram K_2PtCl_6.

$$K_2O = 20.98. \quad Na : K :: 1 : 1.99.$$

(*b*) From salt (*b*).

(1) 0.2753 gram substance gave 0.1526 gram sulphates, and yielded 0.3092 gram K_2PtCl_6.

$$K_2O = 21.68. \quad Na : K :: 1 : 2.14.$$

(2) 0.5876 gram substance gave 0.3256 gram sulphates, and yielded $5/2 \times 0.2675$ gram K_2PtCl_6.

$$K_2O = 21.97. \quad Na : K :: 1 : 2.21.$$

This experiment was supposed to be as nearly as possible a repetition of Barth's, but it did not confirm his results.

Experiment IV.—Six grams of the above salts, 7 grams ethyl iodide, and 12 grams water were heated to 130°–136° for three hours. The contents of the tube were evaporated to dryness the same day, and extracted with alcohol of sp. gr. 0.804. The product was not recrystallized.

Analysis of the products:

(*a*) From salt (*a*).

1.0211 gram substance gave 0.5557 gram sulphates, which gave 5×0.2057 and 5×0.2049 gram K_2PtCl_6.

$$K_2O \begin{cases} 19.45. \\ 19.40 \end{cases} \quad Na : K \begin{cases} 1 : 1.60. \\ 1 : 1.59 \end{cases}$$

(*b*) From salt (*b*).

1.1822 gram substance gave 0.6421 gram sulphates, which gave 5 × 0.2370 and 5 × 0.2363 gram K_2PtCl_6.

$$K_2O \begin{cases} 19.36. \\ 19.30 \end{cases} \qquad Na : K \begin{cases} 1 : 1.58. \\ 1 : 1.57 \end{cases}$$

The ratio of sodium to potassium is the same in the products from both salts. It will be noted that the ratio is different from that in Experiment III, which is 1 : 1.89 and 1 : 2.21. Recrystallization from stronger alcohol increases the ratio.

Experiments V, VI, and VII.—The supposed isomeric potassium sodium sulphites were prepared exactly as for Experiments III and IV.

Analysis of the salts:

(*a*) Salt from acid potassium sulphite and caustic soda.

(1) 0.5527 gram substance gave 0.6090 gram sulphates, yielding 5 × 0.1709 gram K_2PtCl_6.

$K_2O = 29.85$. $Na : K :: 1 : 0.82$.

(2) 0.5051 gram substance gave 0.5588 gram sulphates, yielding 5 × 0.1578 gram K_2PtCl_6.

$K_2O = 30.08$. $Na : K :: 1 : 0.83$.

(*b*) From acid sodium sulphite and caustic potash.

(1) 0.5035 gram substance gave 0.5565 gram sulphates, yielding 5 × 0.1574 gram K_2PtCl_6.

$K_2O = 30.18$. $Na : K :: 1 : 0.84$.

(2) 0.5167 gram substance gave 0.5727 gram sulphates, 5 × 0.1607 gram K_2PtCl_6.

$K_2O = 30.02$. $Na : K :: 1 : 0.82$.

The salts were anhydrous and had practically the same composition.

Experiment V.—The operation was carried on the same as Experiment III, and under the conditions there described.

Analysis of the products:

(*a*) From salt (*a*).

0.3275 gram substance gave 0.1802 gram sulphates, yielding 0.3626 gram K_2PtCl_6.

$K_2O = 21.37$. $Na : K :: 1 : 2.09$.

(*b*) From salt (*b*).

0.2115 gram substance gave 0.1076 gram sulphates, yielding 0.2169 gram K_2PtCl_6.

$$K_2O = 19.80. \quad Na : K :: 1 : 2.10.$$

There is no evidence of isomerism; the ratio of sodium to potassium is nearly as in Experiment III.

Experiment VI.—Ten grams of the double sulphites described above, 11 grams ethyl iodide, and 20 grams water, were heated as in the preceding experiment. The contents of the tube were evaporated to dryness the same day, the residue extracted with 500 cc. alcohol (sp. gr. 0.803) and recrystallized from 250 cc. alcohol of 0.795 sp. gr.

Analysis of the products:

(*a*) From salt (*a*).

0.8606 gram substance gave 0.4710 gram sulphates, and yielded 5×0.1887 gram K_2PtCl_6.

$$K_2O = 21.16. \quad Na : K :: 1 : 2.06.$$

(*b*) From salt (*b*).

0.2361 gram substance gave 0.1297 gram sulphates, and yielded 0.2602 gram K_2PtCl_6.

$$K_2O = 21.28. \quad Na : K :: 1 : 2.01.$$

Experiment VII.—Ten grams of the double sulphites described above, 11 grams ethyl iodide, and 20 grams water, were heated in sealed tubes at the same time as Experiment III. The contents of the tubes were evaporated to dryness the same day. The product was extracted with alcohol of 0.808 sp. gr. and recrystallized from alcohol of 0.803 sp. gr.

Analysis of the products:

(*a*) From salt (*a*).

(1) 0.9116 gram substance gave 0.4978 gram sulphates, yielding 5×0.1910 gram K_2PtCl_6.

$$K_2O = 20.23. \quad Na : K :: 1 : 1.78.$$

(2) 1.0257 grams substance gave 0.5602 gram sulphates, yielding 5×0.2180 gram K_2PtCl_6.

$$K_2O = 20.25. \quad Na : K :: 1 : 1.86.$$

(*b*) From the salt (*b*).

(1) 0.9551 gram substance gave 0.5123 gram sulphates, of which 0.4632 gram gave 5×0.1768 gram K_2PtCl_6.

$K_2O = 19.77$. $Na : K :: 1 : 1.75$.

(2) 1.2675 gram substance gave 0.6916 gram sulphates, yielding 5×0.2617 gram K_2PtCl_6.

$K_2O = 19.93$. $Na : K :: 1 : 1.70$.

No evidence of isomerism.

Conclusion and Summary.

It has been stated that two isomeric potassium sodium sulphites exist, which can be distinguished from each other by their action upon ethyl iodide, the one yielding a salt approaching the composition $4C_2H_5SO_3ONa + KI$, the other approaching $4C_2H_5SO_3OK + NaI$.

Under the most favorable conditions that could be devised, and working on salts supposed to be isomers, in these experiments practically no difference could be observed in the composition of the products obtained by the action of ethyl iodide on the salts. In seven experiments only slight variations could be observed, and this could be explained by changes in the strength of the alcohol.

There appears, therefore, to be no evidence that isomeric potassium sodium sulphites exist.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
December, 1898.

CONDENSATION COMPOUNDS OF AMINES AND CAMPHOROXALIC ACID.

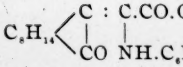
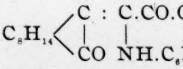
FIFTH COMMUNICATION ON THE INTERACTION OF ETHYLIC OXALATE AND CAMPHOR.[1]

BY J. BISHOP TINGLE AND ALFRED TINGLE.

THEORETICAL.

In the preceding paper on this subject (*loc. cit.*) we described three compounds obtained from aniline and camphoroxalic acid, to which we assigned the formulæ

[1] This JOURNAL, **21**, 238 (1899); *Ibid.*, **20**, 318 (1898); *Ibid.*, **19**, 393 (1897); J. Chem. Soc. (London), **57**, 652 (1890).

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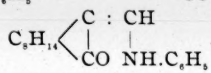
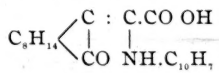


and designated them phenylcamphoformeneaminecarboxylic acid, aniline phenylcamphoformeneaminecarboxylate, and phenylcamphoformeneamine, respectively. We have now obtained a number of other condensation compounds of camphoroxalic acid and its ethylic salt with various aliphatic and aromatic amines, and have gathered further evidence in favor of the above formulæ. The majority of the compounds from aliphatic amines will be described in a subsequent communication and will only be referred to here in so far as is necessary to elucidate theoretical points.

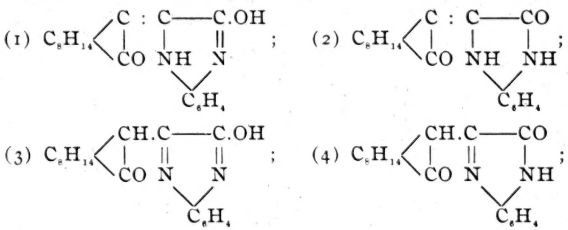
By the action of α-naphthylamine on camphoroxalic acid (as sodium salt), in alcoholic solution, at 100°, under pressure, a compound is obtained crystallizing from benzene in well-developed, transparent, amber-colored crystals; at 100°–105° these gradually become opaque and finally change to a light-brown powder, which, like the crystals, melts and decomposes at 170°. The compound has well-marked acidic properties and readily dissolves in a solution of sodium carbonate; it gives no coloration with ferric chloride and alcohol. This substance is strictly analogous with the first of the aniline compounds mentioned above, and is therefore termed α-naphthylcamphoformeneaminecarboxylic acid,



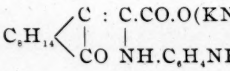
the crystals contain 0.5 molecule benzene of crystallization. The corresponding derivative of β-naphthylamine is formed in an analogous manner; it quickly dissolves in toluene, but in benzene, although its solubility is ultimately considerable, it dissolves very slowly; the supersaturated solution formed on cooling is relatively stable, as crystals are deposited only gradually. The compound is obtained from either solvent in bright-yellow needles melting and decomposing at 173°. In

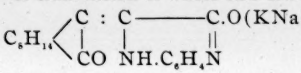
its acidity and other properties it closely resembles the α-naphthyl derivative.

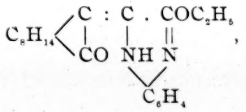
Orthophenylenediamine readily condenses with sodium or potassium camphoroxalate, in equimolecular proportion, when heated at 100°, in alcoholic solution, under pressure. The yield is extremely good. The compound has the formula $C_{18}H_{20}N_2O_2$. It is readily soluble in benzene, and is deposited in bright-yellow needles melting at 246°. It dissolves to some extent in hot water, in boiling hydrochloric acid, and sodium hydrate solution, all of which are practically without action on it. With concentrated sulphuric acid, at the ordinary temperature, a red solution is obtained resembling that produced by a crystal of potassium bichromate. After remaining during eight days without heating the compound is recovered unchanged on dilution, except for the formation of a little resinous matter. The same substance is also formed from orthophenylenediamine and ethylic camphoroxalate under similar conditions. The properties of the compound characterize it as a quinoxaline derivative with one of the following formulæ:



The relationship between 1 and 3, and 2 and 4, respectively, is similar to that between the enolic and ketolic forms of camphoroxalic acid, and may, for present purposes, be ignored, the choice thus falling between 1 and 2. From analogy with the preceding compounds we should expect to obtain from the alkali camphoroxalate as primary, intermediate product a compound of the formula



then, by the further elimination of water this should give rise to the substance  , which on acidification would produce the compound 1. Ethylic camphoroxalate should, in an analogous manner, eliminate water and alcohol successively, and yield the compound 2. We must therefore conclude either that one of these is unstable and immediately changes into the other, or that the excess of diphenylamine employed in the preparation of the ester condensation-product has hydrolyzed the intermediate product,



to the compound 1. We regard the former view as the more probable, since otherwise it is difficult to understand why the ethylic camphoroxalate itself should not have been hydrolyzed. But this would have led to the formation of a phenylenediamine salt which, as no acid was used in the purification, should have been isolated. A second argument, tending in the same direction, is based on the fact that meta- and paraphenylenediamine, under similar conditions, did not hydrolyze the ester at all, although, from their total failure to react in any way, they were present in larger excess than was the ortho-compound. Finally, the yield from the ortho-amine is relatively large, and is scarcely affected by reducing the quantity of amine to somewhat below 1 molecular proportion.

Two substances are formed by the interaction of semicarbazide and potassium camphoroxalate in presence of alcohol, under pressure, at 100°. For the present we will term them simply the α- and β-semicarbazides of camphoroxalic acid. They are separated by means of their different solubility in ether; the α-compound, which readily dissolves, is deposited from acetone in small white needles, melting and decomposing at 218°. It is soluble in a warm solution of sodium carbonate, is reprecipitated in a gelatinous condition on acidification, and gives no coloration with ferric chloride and alco-

hol. The β-derivative is formed in smaller quantity than its companion; it is not soluble in the ordinary neutral organic media, but slowly dissolves in boiling glacial acetic acid, and is gradually deposited from the solution, on the addition of alcohol, in colorless, microscopic needles aggregated into characteristic cubical forms; it melts and decomposes at 209°–210°. The substance resembles the α-derivative in its behavior towards ferric chloride and sodium carbonate, but from solution in the latter, acids precipitate the α-compound. Both bodies agree closely in their content of carbon and hydrogen, which is that required for semicarbazylcamphoformene-carboxylic acid, $C_8H_{14}\begin{cases}C : C.CO.OH \\ | \quad | \\ CO \quad NH.NH.CO.NH_2\end{cases}$; pending further experimental evidence we shall abstain from discussing their relationship and constitution.

We have previously shown (*loc. cit.*) that at 130° ethylic camphoroxalate combines with two molecular proportions of aniline forming phenylcamphoformeneaminecarboxylic anilide, $C_8H_{14}\begin{cases}C : C.CO.NH.C_6H_5 \\ | \quad | \\ CO \quad NH.C_6H_5\end{cases}$. At 100°, under pressure, in alcoholic solution, ethylic camphoroxalate and aniline, or preferably aniline hydrochloride and potassium hydroxide, in the above proportions, yield ethylic phenylcamphoformeneaminecarboxylate, $C_8H_{14}\begin{cases}C : C.CO.OC_2H_5 \\ | \quad | \\ CO \quad NH.C_6H_5\end{cases}$. It readily crystallizes from benzene in white, microscopic needles melting and decomposing at 158°–160°. By the action of alkalies the corresponding acid (m. p. 174°) is obtained. It has been previously prepared by us from aniline and camphoroxalic acid or sodium camphoroxalate.

β-Naphthylamine resembles aniline in its behavior towards ethylic camphoroxalate and yields ethylic β-naphthylcamphoformeneaminecarboxylate, $C_8H_{14}\begin{cases}C : C.CO.OC_2H_5 \\ | \quad | \\ CO \quad NH.C_{10}H_7\end{cases}$. This is somewhat sparingly soluble in boiling benzene, and is deposited in colorless microscopic needles which soften at about

160°, and melt and decompose at 174° when rapidly heated, otherwise at a lower temperature. The compound is insoluble in hot water, and, except for a slight superficial yellow color, unchanged by boiling with a solution of sodium carbonate.

Semicarbazide hydrochloride and ethylic camphoroxalate react in dilute alcoholic solution, at the ordinary temperature, in the presence of potassium acetate. The same product is formed at 100° if potassium hydroxide, in quantity slightly less than is sufficient to liberate the base, is substituted for the acetate.

Ethylic semicarbazylcamphoformenecarboxylate, $C_8H_{14}\begin{cases} C : C.CO.OC_2H_5 \\ | \quad | \\ CO\ NH.NH.CO.NH_2 \end{cases}$, readily dissolves in ethylic acetate, chloroform, and ether; moderately in benzene and acetone, and is practically insoluble in ligroin. It crystallizes from ethylic acetate in colorless needles melting at 202°. When prepared at 100° with potassium hydroxide in the manner referred to above, a second compound is formed in small quantity. This is very sparingly soluble in boiling ether, and in water at the ordinary temperature. It crystallizes in colorless needles and melts at 255°.

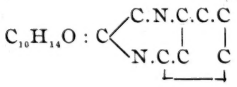
Ethylic camphoroxalate also condenses with ammonia, methylamine, and ethylamine. The compounds formed differ in type from those described above, but resemble the phenylcamphoformeneaminecarboxylic anilide,

$$C_8H_{14}\begin{cases} C : C.CO.NH.C_6H_5 \\ | \quad | \\ CO\ NH.C_6H_5 \end{cases},$$

prepared by heating ethylic camphoroxalate and aniline at 130°, and described by us in the previous paper (*loc. cit.*). The conditions under which they are obtained are similar to those employed for the production of the above ethylic β-naphthylcamphoformeneaminecarboxylate, and, together with the compounds themselves, will be fully detailed in a subsequent communication. At present we merely desire to draw attention to the striking distinction in behavior between the two classes of amines. That this difference is not due

simply to the "aromatic" or "aliphatic" nature of the bases is shown by the behavior of semicarbazide. We regard the difference as being dependent primarily on the basicity of the amine, the strongly basic ones being capable of attacking the carbethoxyl group ($CO.OC_2H_5$) at 100°, aniline only at 130°, whilst the naphthylamines, which are still more feebly basic, are either incapable of reacting with it at all under the conditions we have tried, or at any rate cannot do so at temperatures below that at which ethylic camphoroxalate itself suffers decomposition.

We have hitherto failed to obtain condensation compounds with ethylic camphoroxalate or potassium camphoroxalate, and ethylaniline, dimethylaniline, meta- and paraphenylenediamine, and urea, whilst ethylic camphoroxalate did not react with α-naphthylamine and dimethylamine. We have no explanation to offer for the failure with α-naphthylamine. Perhaps in the case of urea the cause is to be sought in its comparatively feeble basic properties. The inhibition of the reaction in the case of the two phenylenediamines is doubtless due to the relative difficulty experienced in producing rings of seven and eight members,



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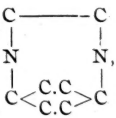
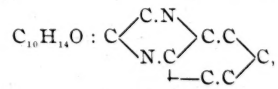


as compared with the six-membered ring,

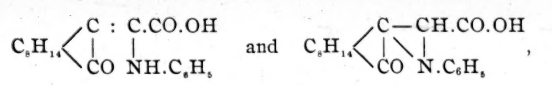


which is actually formed in the case of orthophenylenediamine.

The failure with dimethylaniline is only what would be expected from the nature of the reaction, since, being a tertiary base, there is no hydrogen to form water with the hydroxyl of the ethylic camphoroxalate. The case is otherwise, however, with ethylaniline and dimethylamine. We shall re-

serve the discussion of the latter for a subsequent communication and at present confine ourselves to the former.

In our previous paper on this subject (*loc. cit.*) we suggested two formulæ for phenylcamphoformeneaminecarboxylic acid (m. p. 174°); *viz.*,



expressing our preference for the former. We have obtained crystalline compounds from the corresponding amine (m. p. 166°) with benzoyl chloride, phenylsulphonic chloride, and acetic anhydride. Should further investigation prove these to be simple acyl derivatives the first formula would be established, but in this case there is no very obvious reason why a secondary amine should not react like aniline. The second of the above formulæ, whilst furnishing a satisfactory explanation of the failure of the group R_2NH to react, does not lead us to expect the production of a benzoyl, phenylsulphonyl, or acetyl derivative. Pending further experimental evidence we prefer not to commit ourselves to a decided opinion. It is possible that the chlorides cause cission of the ring, or that, somewhat on the lines of Bischoff's "dynamical theory," stereo-conditions of the two radicals linked to nitrogen prevent the reaction. We hope later to be able to throw light on this point. The compound from benzoyl chloride and phenylcamphoformeneamine mentioned above crystallizes from benzene in prisms resembling those of potassium nitrate, and forming characteristic cruciform aggregates. It melts at 160°–161°. With phenylsulphonic chloride the amine yields a colorless, crystalline compound, which melts at 133° and is insoluble in a solution of sodium hydroxide, indicating the secondary nature of the original amine.

Phenylcamphoformeneamine and acetic anhydride also yield a crystalline product which, after being well drained on tile, melted at 134°. It was, however, contaminated with resinous matter, and repeated recrystallization from alcohol, or preferably ethylic acetate and ligroin, failed to produce a separation, as each crystallization caused some decomposition.

EXPERIMENTAL.

Camphoroxalic Acid and α-Naphthylamine.

Camphoroxalic acid (4.4 gram = 1 mol.), α-naphthylamine (1.4 grams = 0.5 mol.), sodium hydrate (0.8 gram = 1 mol.), and 95 per cent alcohol (about 50 cc.) were heated in a pressure bottle at 100°, during four hours. The alcohol was then evaporated on the water-bath, and the residue treated with water, acidified with dilute sulphuric acid, and extracted with ether. The ethereal solution, after drying with calcium chloride, was distilled, and the residue crystallized twice from benzene. The yield of α-naphthylcamphoformeneaminecarboxylic acid is very good, but is not materially affected by doubling the quantity of amine, as, when this is done, a precipitate of α-naphthylamine sulphate forms on acidifying and hinders the satisfactory extraction of the acid. The crystals deposited from benzene contain 0.5 mol. C_6H_6, and consist of well-developed amber prisms. At 100°–105° they become opaque, and finally change to a yellow powder, which, like the crystals themselves, melt and decompose at 170°.

Analysis:

I. 0.6574 gram substance gave 1.8634 grams CO_2, and 0.3942 gram H_2O.

II. 0.3796 gram substance lost 0.0393 gram at 105°.

	Calculated for $C_8H_{14}\langle C:C.COOH.\frac{1}{2}C_6H_6 \,/\, CO\ NH.C_{10}H_7\rangle$	Found. I.	II.
C	77.32	77.30	....
H	6.70	6.66	....
C_6H_6	10.05	....	10.35

The acid readily dissolves in a solution of sodium carbonate.

Camphoroxalic Acid and β-Naphthylamine.

The experiments in this case were carried out exactly as with the α-amine, and with similar results. In all preparations made with equimolecular proportions of acid and amine a portion of the latter was precipitated as sulphate. Potassium hydrate was found to give better results than sodium hydrate on account of its greater solubility in alcohol. It was observed that sometimes pieces of sodium hydrate did not dis-

solve, and produced a series of small cracks on the inner surface of the glass at the point of their contact with it. This was apparently not the case with potassium hydrate. The crude β-naphthylcamphoformeneaminecarboxylic acid, obtained after the removal of the ether, is purified by quickly extracting it once or twice with hot benzene. It is then recrystallized from toluene and is deposited in bright-yellow needles, melting and decomposing at 173°. The readiness with which it forms supersaturated solutions with benzene has been mentioned above. The yield is excellent.

Analysis:

0.2236 gram substance gave 0.6246 gram CO_2, and 0.1410 gram H_2O.

	Calculated for $C_{22}H_{23}NO_3$.	Found.
C	75.64	76.18
H	6.59	7.00

The slight error in the carbon is doubtless due to the crystals containing a trace of toluene which contains 91.30 per cent of carbon.

Camphoroxalic Acid and Orthophenylenediamine.

The experiments with these compounds were carried out in the same manner as those with the naphthylamines. We found it most convenient not to prepare the free diamine, but to use the hydrochloride together with three molecular proportions of potassium hydrate. The condensation-product does not require to be extracted with ether. It is sufficient to dissolve the alcoholic residue in water, acidify, filter, wash with a little water, and dry the precipitate on a porous plate in the air. After two crystallizations from benzene the compound is deposited in bright-yellow needles melting at 246°. It is slightly soluble in hot water, is practically unchanged by boiling with hydrochloric acid, and is only slightly acted upon by prolonged heating with a solution of sodium hydrate. It dissolves quickly in concentrated sulphuric acid at the ordinary temperature, giving a red coloration, the change being similar in appearance to that produced by potassium chromate under analogous conditions. After remaining during eight

days at the ordinary temperature a white precipitate is obtained on dilution. This rapidly turns yellow and then consists of unchanged crystals. The addition of a crystal of potassium bichromate to the sulphuric acid solution does not produce any characteristic color. If the acid solution is heated alone decomposition gradually takes place. It readily dyes unmordanted cotton bright-yellow. The yield is practically quantitative. The constitution of the compound is discussed in the first part of this paper.

Analyses:

I. 0.2550 gram substance gave 0.6785 gram CO_2, and 0.1590 gram H_2O.

II. 0.1216 gram substance gave 10.8 cc. N at 28°.5 and 741 mm.

	Calculated for $C_{18}H_{20}N_2O_2$.	Found. I.	II.
C	72.97	72.56	....
H	6.76	6.92	....
N	9.46	....	9.64

Semicarbazide and Camphoroxalic Acid.

Semicarbazide hydrochloride (4.4 grams = 2 mols.) was mixed with the acid (4.4 grams = 1 mol.), potassium hydrate (3.4 grams = 3 mols.) and alcohol (95 per cent, 50 cc.) were then added, and the solution heated at 100°, under pressure, during four hours. After removal of the alcohol the residue was acidified with dilute sulphuric or hydrochloric acid and extracted with ether. The acid produced a precipitate which did not dissolve in the ether. It was removed by filtration, dried, and frequently extracted with hot ether. The residue constituted the "β-compound," which is insoluble in all ordinary, neutral, organic media. It was purified by solution in boiling glacial acetic acid. On the addition of alcohol minute microscopic needles are deposited, aggregating into characteristic cubical forms. After repeating this treatment several times the product melts and decomposes at 209°–210°. It readily dissolves in a solution of sodium carbonate, is reprecipitated in a gelatinous condition as the α-derivative on the addition of acid, and gives no coloration with ferric chloride.

The "α-compound" constitutes the residue obtained after the distillation of the combined ethereal solutions mentioned

above. It crystallizes from acetone in small, colorless needles, which melt and decompose at 218°. The substance does not evolve ammonia when boiled with a solution of sodium hydrate. Towards sodium carbonate and ferric chloride its behavior is identical with that of the β-compound.

Analysis:

0.3053 gram substance gave 0.6129 gram CO_2, and 0.1860 gram H_2O.

| | Calculated for $C_8H_{14}\begin{cases} C : C.COOH \\ \quad\quad\quad\

cess was attained by mixing the base and acid with benzene and heating on the water-bath ; some solid separated from the solution, but in quantity too small for further investigation.

Dimethylaniline also gave a negative result when heated with the acid alone at 180°, or with the acid and benzene on the water-bath.

Ethylic Camphoroxalate and Aniline.

Ethylic camphoroxalate (2.5 grams = 1 mol.), aniline hydrochloride (2.6 grams = 2 mols.), potassium hydroxide (1 gram = less than 2 mols.), and alcohol (95 per cent, 50 cc.) were heated together under pressure at 100° during four hours. After removal of the alcohol the residue was treated with water, extracted with ether, and the ethereal solution dried and distilled. The residue, after recrystallizing from benzene, is deposited in almost white, microscopic needles, which melt and decompose at 158°–160°. The yield is excellent.

Analysis :

0.2682 gram substance gave 0.7172 gram CO_2, and 0.1810 gram H_2O.

	Calculated for $C_8H_{14}\begin{cases} C : C.CO.OC_2H_5 \\ \vert \quad\quad \vert \\ CO \quad NH.C_6H_5 \end{cases}$	Found.
C	73.39	72.93
H	7.64	7.49

The compound is therefore ethylic phenylcamphoformeneaminecarboxylate, analogous to the phenylhydrazide previously described by us, and its relationship to the corresponding compound from aniline and camphoroxalic acid is proved by its hydrolysis. When heated for about five minutes with warm 10 per cent aqueous-alcoholic sodium hydroxide in excess, it yields the corresponding acid (m. p. 174°). (Cf. p. 218.) Free aniline may be used for the preparation of the compound instead of the hydrochloride and alkali, but a large excess of the base should be avoided as it hinders crystallization. We have found the above method of working with the amine hydrochlorides and alkalies in slight deficiency very convenient, especially when the free base is unstable or readily volatile ; in the latter case the alkali is conveniently

enclosed in a sealed tube of thin glass, which is broken after the stopper of the pressure bottle has been securely fastened down. We have not observed any perceptible hydrolysis of the ester by the alkali.

Ethylic Camphoroxalate and β-Naphthylamine.

Ethylic β-Naphthylcamphoformeneaminecarboxylate, $C_8H_{14}\begin{cases} C : C.CO.OC_2H_5 \\ | \quad | \\ CO \quad NH.C_{10}H_7 \end{cases}$, was prepared in a similar manner to the phenyl derivative, from β-naphthylamine, and ethylic camphoroxalate in alcoholic solution. Any unchanged amine is removed by means of benzene, and the residue then recrystallized from the same solvent. It is deposited in colorless, microscopic needles, which soften at about 160°, and melt and decompose at 174°, but the melting-point varies according to the rapidity with which the bath is heated. The compound is not affected by boiling water nor by boiling aqueous sodium carbonate except for the production of a superficial yellow color.

Analysis:

0.3392 gram substance gave 0.9446 gram CO_2, and 0.2242 gram H_2O.

	Calculated for $C_{24}H_{27}NO_3$.	Found.
C	76.39	75.94
H	7.16	7.34

No definite compound could be isolated except apparently unchanged naphthylamine, by heating ethylic camphoroxalate with β-naphthylamine at 140°–145° during three hours.

Ethylic Camphoroxalate and Semicarbazide.

Ethylic Semicarbazylcamphoformenecarboxylate, $C_8H_{14}\begin{cases} C : C.CO.OC_2H_5 \\ | \quad | \\ CO \quad NH.NH.CO.NH_2 \end{cases}$, is prepared by heating the ester with semicarbazide hydrochloride (3 mols.), potassium acetate (3.5 mols.), and alcohol (95 per cent), at 100°, under pressure, during four hours, or by allowing the substances to remain at the ordinary temperature in dilute alcoholic solution

during seven days. In the former case the compound was extracted by means of ether; in the latter it separated on dilution with water. It is readily soluble in ethylic acetate, chloroform, and ether, moderately so in benzene and acetone, and sparingly in ligroin. It is deposited from ethylic acetate in colorless needles, melting at 202°. The yield is good whichever method of preparation is employed. In one experiment, carried out at 100°, a compound was obtained in small quantity, which did not dissolve in either the ethereal or aqueous layers of liquid, nor in any organic solvent we could employ. It crystallized in needles, melted at 255°, and may be semicarbazide sulphate, as the aqueous solution had been acidified with dilute sulphuric acid. Neither J. Thiele and O. Strange,[1] who first prepared this salt, nor F. Tiemann and P. Krüger,[2] who subsequently employed it, give the melting-points of their preparations.

Analyses:

I. 0.4832 gram substance gave 1.0056 grams CO_2, and 0.3360 gram H_2O.

II. 0.4532 gram substance gave 0.9438 gram CO_2, and 0.3234 gram H_2O.

III. 0.1540 gram substance gave 19.4 cc. N_2 at 27° and 746.6 mm.

	Calculated for $C_{18}H_{23}N_3O_4$. (Mol. wt. = 309.)	Found. I.	Found. II.	Found. III.
C	58.25	56.75	56.79	....
H	7.44	7.72	7.92	....
N	13.59	....	....	13.64

Molecular weight determinations:

Solvent, phenol.

Weight of solvent. Grams.	Weight of substance. Gram.	Δ.	*m*.
19.6330	0.1145	0.19°	227
19.6330	0.2220	0.36°	232.5

Ethylic Camphoroxalate and Orthophenylenediamine.

The ester reacts with the orthodiamine hydrochloride and

[1] Ber. d. chem. Ges., **27**, 34.

[2] *Ibid.*, **28**, 1754.

sodium hydrate, in presence of alcohol, at 100°, under pressure. The product was isolated by evaporating off the alcohol and washing with water. Its appearance and melting-point proved it to be identical with the corresponding compound from sodium camphoroxalate. In the first experiments two molecular proportions of amine hydrochloride, together with the equivalent amount of sodium hydrate, were employed; subsequently, in order to avoid any chance of hydrolysis, exactly equimolecular proportions of the ester and amine were taken, with a small deficiency of sodium hydrate, but without appreciably affecting the result. The yield is large.

Unsuccessful Experiments with Ethylic Camphoroxalate.

Meta- and paraphenylenediamine yielded only tarry matter when treated with ethylic camphoroxalate under the same conditions as the ortho-compound. A similar result was obtained in the case of α-naphthylamine, both at 100° under pressure, and at 140°–145°. In both experiments the only products which could be isolated were the original materials. Ethylaniline, both as free base and as hydrochloride, together with sodium hydrate, and dimethylaniline in the free state, at 100°, under pressure, in alcoholic solution, also failed to give any condensation-products.

Experiments with Phenylcamphoformeneamine.

Benzoyl chloride reacts with phenylcamphoformeneamine, in presence of a little sodium hydrate, either when gently warmed or at the ordinary temperature if allowed to remain during thirty-six hours. The latter appears to be the preferable method. The product was well washed with a solution of sodium carbonate, extracted with ether, the ether dried and removed, and the residue recrystallized from benzene. The compound is deposited in cruciform aggregates of prisms resembling potassium nitrate in appearance, and melting at 160°–161°. It has not yet been further investigated. An attempt to prepare it by the ordinary Schotten-Baumann method, in aqueous solution, was not successful, as benzoic acid was the only product that could be isolated in quantity.

Phenylsulphonic chloride does react with the amine by the

Schotten-Baumann method, but when the two are simply heated together they only yield an oil. The product has as yet only been obtained in small amount. It is readily deposited from benzene in colorless needles, melts at 133°, and does not dissolve in a solution of sodium hydrate.

The amine, when boiled with 10 molecular proportions of acetic anhydride during fifteen minutes, yields a brown liquid, which deposits a gummy substance after treatment with a solution of sodium carbonate. Recrystallization from a mixture of ethylic acetate and ligroin yields colorless crystals, which, after draining on a porous plate, melted at 134°. The crystals were always accompanied by resinous matter, and, as repeated recrystallizations failed to effect any separation of the two, further attempts to purify the compound were abandoned. We propose to continue this work in various directions.

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A METHOD FOR THE DETERMINATION OF THE MELTING-POINT.

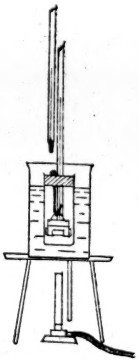
BY M. KUHARA AND M. CHIKASHIGE.

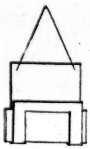
Several different methods have hitherto been suggested for determining the melting-point of substances. One of these, that now in common use, consists in heating the substance to be experimented upon in a capillary tube, fastened to a thermometer, and immersed in a bath. It is usual, in this case, to take the temperature at which the substance begins to melt away from the walls of the capillary tube as its melting-point. This method, however, is very liable to give too high results, as it is difficult to observe the exact point of fusion of that portion of the substance which is in contact with the walls of the tube, before the inner portion thereof reaches its melting-point; this is apparently higher than the real melting-point, owing to the bad conductivity of the air contained in the interstices of the substance, and the consequent overheating. We also find another disadvantage in this method; namely, that substances which cannot be pulverized, such as

waxes, fats, etc., are, with difficulty, introduced into the capillary tube.

We have recently devised a method which, we think, will eliminate all the disadvantages of the tube method, and which, moreover, can easily be carried out in chemical laboratories.

In this new method, instead of a capillary tube, we make use of a pair of cover-glasses for microscopical purposes, cut in halves, between which the substance to be tested is introduced, either in powder, in crystals, or in thin slices. If the substance is in the state of powder, we can make the layer as





thin as possible by pressing and sliding the two pieces with the fingers, so that the heat of the bath may at once be conducted throughout the whole mass. The surface exposed is very large compared with the quantity of the substance taken, and, consequently, its behavior towards heat can be distinctly observed. Before the substance is melted the glass appears opaque, while it becomes transparent when fusion occurs. The thinner the layer the more distinct is the difference ; but with volatile substances, a quantity somewhat in excess of what is apparently essential should be taken, in order to make allowance for loss by volatilization.

The pair of glass-pieces is then fastened to a holder made

of platinum foil and tied, if necessary, with a piece of fine wire of the same material. The holder, which can easily be made by folding the foil and cutting it with scissors, as shown in the annexed figure, is suspended in a wide test-tube, into which is inserted a thermometer close to the holder. The test-tube, serving as an air-bath, is immersed in the sulphuric-acid bath almost to its mouth. The further steps of the process require no modification of the old methods.

The glass pieces can be used any number of times, unless they are broken; this is considered another advantage over the tube method.

The result of experiments with our method is given in the following table. The substances taken were purified by repeated crystallization, and the temperatures given are the corrected ones:

Substance.	Exp. I.	Exp. II.	Exp. III.	Mean.	M. P. already known.	Observer.
Chloral hydrate	57°.3	57°.3	57°.0	57°.2	57°	Meyer and Dulk
Urea	132°.1	132°.1	132°.3	132°.2	132°	Lubavin
Phthalic acid	203°.2	202°.7	203°.0	203°.0	203°	Ador
Phthalimide	233°.6	233°.7	233°.6	233°.6	233°.5	Graebe

The melting-point of phthalic acid has been a subject of discussion, the figures given by different observers differing considerably. Lossen[1] gives it as low as 184°, but Ador[2] states that crystallized phthalic acid melts at 213° and the powdered substance at 203°. Remsen[3] ascribes the variation to the fact that phthalic anhydride, formed partly from the acid, lowers the melting-point of the mixture. In order to test his view, small quantities of the acid, introduced into a U-tube, were heated over a paraffin-bath at the temperatures of 140° and 170°, and the melting-point was found to be considerably lower in both cases. This experiment was conducted by one of us a number of years ago, when working in his laboratory. We have found, however, with the new method, that both the crystallized and the powdered substances melt at the same constant temperature of 203°, whether the air-tube is grad-

[1] Ann. Chem. (Liebig), **144**, 76.
[2] *Ibid.*, **163**, 230.
[3] This JOURNAL, **8**, 30.

ually heated or plunged at once into the bath at a temperature above 205°. This is probably due to the fact that the anhydride formed is freely volatilized in our apparatus through the interstices of the two glass-pieces, and the remaining acid, kept pure, melts at its proper temperature. With our method we have never observed a temperature so high as 213°, nor so low as 184°, while with the capillary-tube method we often noted a melting-point as low as 185°.

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THE SYMMETRICAL CHLORIDE OF PARANITRO-ORTHOSULPHOBENZOIC ACID.[1]

BY F. S. HOLLIS.

Introduction.

The present investigation may be divided into two parts. The first consists of further work on the method of preparation and separation of the chlorides of paranitroorthosulphobenzoic acid. This work was confined largely to the unsymmetrical or low-melting chloride, as this is the one used mainly in the second part of the investigation. The preparation of the unsymmetrical dichloride, first obtained by Remsen and Gray,[2] was found to be a matter of considerable difficulty and uncertainty, unless the crystallization could be conducted out of doors at a very low temperature.

As the result of a series of experiments, undertaken to determine the best conditions for the preparation of the unsymmetrical chloride, a method has been devised by which the unsymmetrical chloride can be prepared in any desired quantity in the laboratory.

The second part of the investigation consists of a study of the action of benzene and aluminium chloride on the chlorides under varying conditions, and the preparation of a series of derivatives of the product formed.

[1] From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University, June, 1896, for the degree of Doctor of Philosophy. The investigation was undertaken at the suggestion of Professor Remsen and was carried on under his guidance.

[2] This JOURNAL, **19**, 496.

Remsen and Saunders[1] and Remsen and McKee,[2] working with the chlorides of orthosulphobenzoic acid, found that the action of benzene and aluminium chloride gives the same products with both chlorides.

It was thought that, on account of the greater stability of the paranitroorthosulphobenzoic acid, the action of benzene and aluminium chloride might lead to the formation of two series of derivatives, one derived from the symmetrical chloride and the other from the unsymmetrical chloride, in which the resulting compound would retain the unsymmetrical structure of the chloride. This proved not to be the case, as the product of the action of benzene and aluminium chloride on both of the chlorides was found to be paranitroorthobenzoylbenzenesulphone chloride.

It was found that paranitroorthosulphobenzoic acid does not yield a sulphone corresponding to the one obtained from orthosulphobenzoic acid by Remsen and Saunders,[3] although the reaction was conducted under the conditions used by them, as well as under a variety of different conditions.

Preparation of Material.

The acid potassium salt of paranitroorthosulphobenzoic acid was prepared from paranitrotoluene according to the method described by Kastle,[4] and used later by Remsen and Gray.[5]

One thousand grams of paranitrotoluene gave 1439 grams of the neutral potassium salt of paranitrotolueneorthosulphonic acid. One thousand grams of the potassium salt of paranitrotolueneorthosulphonic acid gave 800 grams of the acid potassium salt of paranitroorthosulphobenzoic acid.

The Action of Phosphorus Pentachloride on the Acid Potassium Salt of Paranitroorthosulphobenzoic Acid.

The action of phosphorus pentachloride on the anhydrous acid potassium salt of paranitroorthosulphobenzoic acid gives rise to the formation of an unsymmetrical and a symmetrical dichloride, as determined by Remsen and Gray,[6] according to the following equations :

1 This JOURNAL, **17**, 355.
2 *Ibid.*, **18**, 794.
3 *Loc. cit.*
4 This JOURNAL, **11**, 177.
5 *Loc. cit.*
6 *Loc. cit.*

$$C_6H_3\begin{cases}COOH\\SO_2OK\\NO_2\end{cases} + 2PCl_5 = C_6H_3\begin{cases}CCl_2{>}O\\SO_2\\NO_2\end{cases} + 2POCl_3 + HCl + KCl.$$

$$C_6H_3\begin{cases}COOH\\SO_2OK\\NO_2\end{cases} + 2PCl_5 = C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases} + 2POCl_3 + HCl + KCl.$$

Remsen and Gray[1] found that the relative amount of each chloride depends on the temperature and length of time which the phosphorus pentachloride is allowed to act on the acid potassium salt. The largest amount of the unsymmetrical chloride, amounting to 80 or 90 per cent of the total, was formed by heating a mixture of 2 molecules of phosphorus pentachloride and 1 molecule of the anhydrous acid potassium salt to 150° C. for four or five hours in a distilling-bulb, immersed in a sulphuric-acid bath.

Under these conditions, the amount of symmetrical chloride formed amounted to 10 or 20 per cent of the total, but this is increased to 30 per cent by heating in an open dish on a water-bath. The symmetrical chloride was separated by using chloroform as a solvent.

As considerable difficulty was experienced, mainly in the preparation of the unsymmetrical chloride, according to the directions given by Remsen and Gray, a series of experiments was made under different conditions with amounts of the acid potassium salt varying from 20 to 60 grams in order to determine the conditions most favorable for the formation of the unsymmetrical chloride. The results of these experiments are embodied in the following method.

a. The Preparation of the Unsymmetrical Chloride.—A mixture of 1 molecule of the acid potassium salt, previously heated to 150° C. for four hours, and 2.5 molecules of phosphorus pentachloride is carefully ground together in a mortar and introduced into a distilling-bulb having a capacity of about six times that of the volume of the mixture. The outlet tube of the bulb is closed, and a cork, through which runs a glass tube about 3 feet long, the lower end reaching nearly to the surface of the mixture, inserted in the neck.

[1] *Loc. cit.*

The distilling-bulb, thus closed, is immersed in a sulphuric-acid bath, previously heated to 150° C., and this temperature maintained for five hours.

No reaction takes place on mixing the acid potassium salt and the phosphorus pentachloride, but upon immersing the bulb containing the mixture in the heated bath, vigorous action begins immediately, and the resulting phosphorus oxychloride is conducted back upon the product by means of the condensing-tube. The temperature of 150° C. cannot safely be exceeded, as decomposition of the chloride begins at 160° C.

At the end of five hours the tube is removed from the neck of the flask, the perforated stopper replaced by a solid one, the outlet tube opened, and the phosphorus oxychloride distilled off.

The resulting chloride, which is in the form of a thick, yellow, oily liquid, is poured into a large bottle, nearly filled with cold water, and shaken vigorously so as to break it into small globules. This washing is continued until the chloride hardens to a solid cake, which commonly takes place after washing with five or six successive portions of cold water. The solidified chloride is broken up and dried by pressing between filter-paper, and in this form it may be exposed to the air without undergoing much, if any, decomposition.

By using 2.5 molecules of phosphorus pentachloride, all of the acid potassium salt is converted into the form of the chloride, while, if but 2 molecules are used, varying amounts of the acid potassium salt, in some cases as much as 25 per cent, are unacted upon and may be recovered from the wash-water.

The product obtained by this method consists, with the exception of slight impurities, of only the unsymmetrical chloride, thus making the crystallization from chloroform unnecessary. One hundred grams of anhydrous acid potassium salt gave, on an average, 99 grams of the crude unsymmetrical chloride.

Previous work showed that the crystallization of the unsymmetrical chloride from ligroin (50°–80°) was a difficult matter, unless it could be done out of doors during very cold weather. The same was found to be the case with the un-

symmetrical chloride of orthosulphobenzoic acid by Remsen and Saunders.[1]

A solution of the crude chloride in purified ligroin (50°–80°), on standing out of doors at a temperature of 6° F., crystallized in clusters of crystals, some of which measured 3 centimeters in length. An attempt was made to obtain the chloride in the form of crystals by cooling the ligroin solution to 0° C. in a refrigerating box, such as was used by Remsen and McKee.[2] The chloride invariably separated as an oil, and no advantage was derived by drawing a current of cold, dry air through the flask containing the ligroin solution. Some of the oily chloride which separated from the ligroin solution, and from which the ligroin had been decanted, formed an opaque semisolid mass on placing it in a freezing-mixture, but no crystals were deposited.

The first indication of crystallization in the laboratory was obtained on placing some of the oil, which had been dissolved several times in fresh portions of hot ligroin (50°–80°) and allowed to separate out on cooling, in a freezing-mixture, and stirring with a rod. This suggested the possibility that some material, which by its presence retards crystallization, had been dissolved out of the mass by the several portions of ligroin in which it had been dissolved. This was shown to be the case by several tests, and gave rise to the following method of purification and crystallization, in which the further change is made of using ligroin of boiling-point 90°–125° as the solvent. This ligroin is to be preferred to that having a lower boiling-point, as the chloride is apparently much more soluble in it, and crystallizes from the solution at the temperature of the laboratory. The ligroin is purified by shaking in a separating-funnel with concentrated sulphuric acid until it imparts no color to a fresh portion of acid, after which it is treated with a solution of caustic soda to neutralize the acid, and washed free from alkali by water.

The crude chloride, which is always somewhat dark colored and gummy, is placed in an Erlenmeyer flask with purified ligroin (50°–80°) and washed by stirring it with a rod until it yields a granular powder having but little color.

[1] *Loc. cit.* [2] *Loc. cit.*

On boiling the chloride thus purified with ligroin (90°–125°), it dissolves, with the exception of slight remaining impurities, and on cooling the solution becomes cloudy, and the excess of chloride separates out as a light-colored oil. It is best to decant the solution from the separated oil after separation has mainly ceased at the temperature at which crystallization is to proceed, but before the solution has become clear. The chloride is obtained from this solution at the temperature of the laboratory in clusters of needles having the form of long monoclinic prisms as observed by Remsen and Gray.[1] The rate of crystallization is increased by keeping the solution at a lower temperature, but no especial advantage is derived unless the temperature is very low, when larger crystals are obtained. The crystals of the chloride thus obtained have a constant melting-point of 57° C. (uncorr.).

The purified chloride which separates from the ligroin as an oil generally crystallizes on standing, but it is better to redissolve it in a fresh portion of ligroin, by which it is further purified, and proceed according to the directions given above.

The principal impurity which causes difficulty in the crystallization of the unsymmetrical chloride seems to be that which is removed by the preliminary treatment with ligroin (50°–80°).

On evaporating the ligroin used in washing the chloride, this impurity remains as a dark-colored, slightly viscous liquid having a strong acid reaction. It showed no tendency to crystallize after standing in the laboratory for five months. A small amount of another impurity was obtained as a flocculent material on dissolving the crude chloride in chloroform. It melts after purification at 100°–105° C., and is probably the anhydride.

b. The Preparation of the Symmetrical Chloride.—One portion of the symmetrical chloride was made in order to test the action of benzene and aluminium chloride, but no comparative tests were made, as in the case of the unsymmetrical chloride. The method used for its preparation differed somewhat from that of Remsen and Gray.

[1] *Loc. cit.*

The conditions chosen for its preparation were, as far as possible, the opposite of those found to be most favorable for the formation of the unsymmetrical chloride.

The anhydrous acid potassium salt and phosphorus pentachloride, in the proportion of 1 molecule of the former to 2 molecules of the latter, are mixed by grinding them together, and the action commenced by placing the vessel containing the mixture in a sulphuric-acid bath previously heated to 150° C.

The vessel is removed from the bath as soon as the action commences, and allowed to stand until the action is complete, which requires about ten minutes.

The mass is washed, as in the case of the unsymmetrical chloride, by shaking in a bottle with five or six portions of cold water.

The chloride thus washed exists in the form of a light-colored, thick gum. It is dissolved in anhydrous chloroform, the solution dried by means of calcium chloride, and allowed to stand at the temperature of the laboratory. Crystals of the symmetrical chloride are formed only after the chloroform has nearly all evaporated, and crystallization proceeds very slowly.

The chloride was obtained in the form of small monoclinic crystals, having a constant melting-point of 94° C. (uncorr.).

The yield indicated that, under the conditions used, the action of the phosphorus pentachloride is complete, but between 35 and 40 per cent of the product obtained consists of the symmetrical chloride.

The Action of Benzene and Aluminium Chloride on the Chlorides of Paranitroorthosulphobenzoic Acid.

a. The Action on the Unsymmetrical Chloride.—When aluminium chloride is added to a solution of the unsymmetrical chloride in benzene, slight action begins immediately, as is shown by the darkening of the color of the solution and a slight evolution of hydrochloric acid gas.

In the case of small quantities of the chloride, heated with an excess of aluminium chloride, the reaction is complete in from fifteen to twenty minutes. A series of experiments was

made in order to determine the best conditions for conducting the reaction and for separating and purifying the product.

Under some conditions the product contains a considerable amount of a dark-purple material which separates as an impurity on crystallization. As a result of these experiments, the following method was adopted :

Twenty grams of the unsymmetrical chloride is dissolved in 100 cc. of benzene in a flask provided with a return-condenser, and about 10 grams of aluminium chloride in small pieces added. This is heated with a small flame for from one to two minutes, at the end of which time vigorous action commences and continues without further heating for ten minutes.

After the action is over the flask is heated repeatedly so as to maintain an even evolution of hydrochloric acid gas for about eight minutes, at the end of which the reaction is complete. The resulting product is poured into 750 cc. of water in a liter separating-funnel, 75 cc. of hydrochloric acid (sp. gr. 1.12) added and the mixture well shaken.

After the benzene layer has risen the water is drawn off and the small amount of the product suspended in it separated by filtration. The greater part of the product is in the form of a pinkish-white powder, which remains in suspension in the benzene, from which it is separated by filtration, dried, and purified with the portion obtained from the water. The product is purified by dissolving in benzene and adding rather more than an equal volume of anhydrous ether, which causes a more rapid crystallization. By this method it is obtained in clusters of small, apparently monoclinic crystals, having a rhombohedral habit, or as a granular powder if crystallization takes place rapidly.

Some of the larger crystals measured 4 or 5 mm. on an edge. The larger crystals have a purple or green color, and the granular form is generally slightly green. Both forms yield a white powder. The pure crystalline product has a constant melting-point of 177° C. (uncorr.).

The portion of the product which remains in solution in the benzene is mixed with a small amount of the purple impurity before described, but it is obtained in a crystalline form of fair purity by drying the benzene solution, evaporating it

to about one-third of its volume, and adding rather more than an equal volume of absolute ether. The dark impurity may be largely removed by washing with absolute alcohol, in which it dissolves readily.

An attempt was made to prevent the darkening of the benzene solution during evaporation by conducting the evaporation in a current of sulphur dioxide, as it was believed that the darkening was due, in part at least, to the action of the air.

The product was not materially improved, and a certain amount of free acid was always found to be present after such treatment. The rapid evaporation of the dried benzene solution and the addition of an equal volume of absolute ether to insure rapid crystallization is greatly to be preferred.

Twenty grams of the unsymmetrical chloride gave 16 grams of the product as first obtained. This was slightly decreased by recrystallization.

The product has a characteristic disagreeable odor.

b. The Action on the Symmetrical Chloride.—The reaction was conducted exactly as in the case of the unsymmetrical chloride, the same relative quantities and method of treatment being used. The method of separation was also the same.

The product gave, on purification, crystals of the same form, size and color as those obtained from the unsymmetrical chloride.

The melting-point of the purest crystals is also the same, 177° C. (uncorr.).

Two grams of the symmetrical chloride gave 1.5 grams of the product.

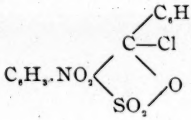
Analyses of the product of the action of benzene and aluminium chloride on the unsymmetrical chloride:

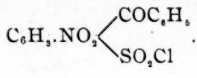
0.2051	gram	gave	0.3632	gram	CO_2
0.2992	"	"	0.5249	"	"
0.1994	"	"	0.0535	"	H_2O
0.2992	"	"	0.0819	"	"
0.2508	"	"	9.03	cc.	N
0.3496	"	"	12.88	"	"
0.2601	"	"	0.1957	gram	$BaSO_4$
0.2058	"	"	0.1584	"	"
0.2602	"	"	0.1888	"	"

0.2492 gram gave	0.1878 gram	$BaSO_4$
0.2424 " "	0.1811 "	"
0.2434 " "	0.1072 "	AgCl
0.2058 " "	0.0925 "	"
0.2602 " "	0.1161 "	"

	Calculated for $C_{19}H_{13}O_5NSCl$.	Found. I.	II.	III.	IV.	V.
C	47.92	48.29	47.84	....	....	....
H	2.45	2.97	3.04	....	....	....
N	4.30	4.32	4.42	....	....	....
S	9.83	10.33	10.56	9.96	10.34	10.26
Cl	10.90	10.90	11.11	11.03	....	....

The two following structural formulæ are possible for a substance derived from the unsymmetrical chloride, and having the composition indicated by the analyses.





The fact that the product is apparently not acted upon by alcoholic potash, together with its high melting-point and its properties generally favor the belief that it has the structure represented by the first.

The formation of the same product by the action of benzene and aluminium chloride on the symmetrical chloride seems to indicate that the product derived from each chloride is paranitroorthobenzoylbenzenesulphone chloride. This view agrees with the results obtained by the action of benzene and aluminium chloride on orthosulphobenzoic acid by Remsen and Saunders[1] and Remsen and McKee.[2]

It is clear from the analysis that but one of the chlorine atoms of the chloride is replaced by this reaction. All attempts to prepare the diphenyl derivative or paranitroorthobenzoylbenzenesulphone were unsuccessful, although the conditions were varied widely, both as to temperature and the length of time which the heating was continued.

The conditions already described give the best yield and also the purest product.

[1] *Loc. cit.* [2] *Loc. cit.*

By allowing the mixture to stand for a day with occasional heating nearly to the boiling-point of the benzene, similar good results are obtained.

By heating to the boiling-point of benzene, for three hours, using a return-condenser, the yield is decreased, and a large amount of a black, tarry matter obtained, which is almost insoluble in benzene. This dissolves readily in absolute alcohol, from which solution it is precipitated as a dark red-colored powder on adding water, and after being thrown out of solution in this way, it becomes less soluble in absolute alcohol.

It swells up on heating and gives an odor like that obtained on burning sulphonic acids. On burning off the organic portion a considerable amount of alumina remains. Hydrochloric acid dissolves the alumina, leaving the organic portion in the form of a black, tarry mass.

The Action of Hydrochloric Acid on Paranitroorthobenzoylbenzenesulphone Chloride.

a. The Action of Dilute Hydrochloric Acid (sp. gr. 1.12).—The action of dilute hydrochloric acid was determined by boiling the sulphone chloride in a flask, provided with a return-condenser, with an excess of the acid until it was all dissolved, which usually requires about six hours. The solution is then filtered and evaporated on a water-bath, and the heating continued until no odor of hydrochloric acid remains. The resulting acid is obtained in the form of a dark, solid substance, which dissolves readily in water and takes up water on standing in the air.

Barium Salt.—The barium salt was prepared by adding barium carbonate to a solution of the acid in water, filtering off the excess of barium carbonate, and evaporating the solution under a bell-jar by means of a current of dry air. The solution cannot be concentrated safely by boiling, as it causes a decomposition of the salt.

The salt was obtained in the form of small, light-colored crystals, arranged in tufts.

In the following analyses of salts, the base, as well as the sulphur, is calculated on the basis of the anhydrous salt.

I. 0.2039 gram substance lost 0.0119 gram at 180° C., and gave 0.0586 gram $BaSO_4$.

II. 0.2892 gram substance lost 0.0179 gram at 180° C., and gave 0.0810 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 3H_2O$.	Found. I.	II.
H_2O	6.72	5.84	6.18
Ba	18.29	18.12	17.65

The barium salt of another portion of acid, prepared in the same way, was obtained in the form of short, thick, monoclinic prisms, which seemed to be made up of a series of plates.

I. 0.2010 gram substance lost 0.0260 gram at 210° C., and gave 0.0557 gram $BaSO_4$.

II. 0.2021 gram substance lost 0.0250 gram at 210° C., and gave 0.0562 gram $BaSO_4$.

III. 0.2263 gram substance gave 0.1262 gram $BaSO_4$.

IV. 0.2109 gram substance gave 0.1201 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 6H_2O$.	Found. I.	II.
H_2O	12.60	12.93	12.66
Ba	18.29	18.64	18.70
S	8.54	8.76	8.93

This salt became opaque on standing in a specimen tube for one month, due to the loss of water of crystallization.

0.2133 gram of the opaque salt lost 0.0139 gram at 210° C.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 3H_2O$.	Found.
H_2O	6.72	6.56

The results of the analysis indicate that paranitroorthobenzoylbenzenesulphone chloride is converted into paranitroorthobenzoylbenzenesulphonic acid by boiling with dilute hydrochloric acid, according to the following equation:

$$C_6H_3NO_2\begin{cases}COC_6H_5\\SO_2Cl\end{cases} + H_2O = C_6H_3NO_2\begin{cases}COC_6H_5\\SO_2OH\end{cases} + HCl.$$

b. The Action of Concentrated Hydrochloric Acid (sp. gr. 1.17).—The action of concentrated hydrochloric acid was determined by heating the sulphone chloride with a large excess of acid in a sealed tube.

The tube was first heated for six hours in a water-bath, but, as no action seemed to take place, it was transferred to a Carius furnace and heated for six hours at a temperature of 175° C. The substance dissolved, with the exception of a few dark flakes, and the acid was colored brown. The flakes were removed by filtration, the acid solution evaporated to dryness on a water-bath, and the heating continued until the resulting acid had no odor of hydrochloric acid. The barium salt was prepared as in the case of the acid derived from the sulphone chloride by the action of dilute hydrochloric acid. It crystallized in the form of light-colored, fine needles, which were arranged in loose tufts or clusters. A few darker crystals in the form of larger monoclinic crystals with rhombohedral habit were obtained from the mother-liquor.

I. 0.2103 gram of the needles lost 0.0164 gram at 210° C., and gave 0.0609 gram $BaSO_4$.

II. 0.2083 gram of the needles lost 0.0158 gram at 210° C., and gave 0.0595 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 3\frac{1}{2}H_2O$.	Found. I.	Found. II.
H_2O	7.75	7.69	7.59
Ba	18.29	18.21	18.20

0.1053 gram of the larger, dark crystals lost 0.0152 gram at 210° C., and gave 0.0279 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 7H_2O$.	Found.
H_2O	14.40	14.43
Ba	18.29	18.20

The Action of Dilute Sulphuric Acid on Paranitroorthobenzoylbenzenesulphone Chloride.

The action of sulphuric acid on the sulphone chloride was determined by heating in a flask with a return-condenser until it dissolved. The resulting product was an acid, which was converted into the barium salt by adding an excess of barium carbonate, as in the previous experiments.

The barium salt was obtained in the form of short needles arranged in clusters.

0.1943 gram substance lost 0.0119 gram at 180° C., and gave 0.0570 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 3H_2O$.	Found.
H_2O	6.72	6.12
Ba	18.29	18.48

The Action of Water on Paranitroorthobenzoylbenzenesulphone Chloride.

The action was determined by boiling the sulphone chloride in a flask with a return-condenser until it dissolved. It was necessary to boil somewhat longer to dissolve the substance than in the experiments in which acids were used.

The resulting product was an acid which, by treating in the usual way with barium carbonate, gave a barium salt which crystallized in well-formed monoclinic crystals.

0.1610 gram substance lost 0.0207 gram at 210° C., and gave 0.0443 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 6H_2O$.	Found.
H_2O	12.60	12.85
Ba	18.29	18.56

The Action of Absolute Alcohol on Paranitroorthobenzoylbenzenesulphone Chloride.

The action of absolute alcohol on the sulphone chloride was determined by boiling in a flask with a return-condenser until it dissolved. It dissolved rather more rapidly than in the experiments in which acid was used, and the boiling was continued for a short time after all the material was dissolved. After a part of the alcohol was evaporated, a few drops of the solution showed indications of crystallization on evaporating rapidly on a watch-glass, but, on further evaporation, the solution darkened and the resulting product was an acid as in the previous experiments.

The barium salt was prepared as in the previous experiments. The crystals first obtained were in the form of small, light-colored needles arranged in clusters, but later well-formed monoclinic crystals were obtained from the same solution.

0.1957 gram of the needle-shaped crystals lost 0.0153 gram at 210° C., and gave 0.0559 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 3\frac{1}{2}H_2O$.	Found.
H_2O	7.75	7.81
Ba	18.29	18.21

0.2007 gram of the larger crystals lost 0.0285 gram at 210° C., and gave 0.0535 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 7H_2O$.	Found.
H_2O	14.40	14.26
Ba	18.29	18.27

The above analyses indicate that the action of dilute or concentrated hydrochloric acid, sulphuric acid, water and alcohol on paranitroorthobenzoylbenzenesulphone chloride converts it into paranitroorthobenzoylbenzenesulphonic acid.

Comparison of the Barium Salts.

The analyses of the barium salt of the acids, derived from the action of the various substances on the sulphone chloride, show that the acid is in every case the same and that the salts contain the same amount of barium when calculated upon the basis of the anhydrous salt. The amount of water of crystallization varies widely in the different salts, depending on the conditions under which crystallization takes place.

The needles are obtained from the more concentrated solutions, and crystals of this form are first obtained from a solution which has been evaporated by heating before placing it under a bell-jar. All crystals having this form contain 3 or 3.5 molecules of water of crystallization.

The larger monoclinic crystals which form in the same solution after the formation of needles ceases, or when a cold solution is evaporated to the point of crystallization under a bell-jar, contain 6 molecules of water of crystallization. On exposure to the air or even in a stoppered tube these lose water of crystallization and become opaque.

The only analysis made of a crystal that had changed in this way shows that it contains 3 molecules, while it crystallized with 6.

Those crystals which contain 7 molecules of water of crystallization are obtained on slow crystallization, on standing in the air, from a dilute solution or from a mother-liquor from

which crystals containing a less amount of water of crystallization have been deposited.

Although all the barium salts containing different amounts of water of crystallization appear to crystallize in the monoclinic system, they show clearly a variation in form.

Owing to lack of time, no comparative study could be made of the relation existing between the amount of water of crystallization and the crystallographic constants.

The barium salt of paranitroorthobenzoylbenzenesulphonic acid is characterized by an intense bitter taste.

Preparation of Other Salts from the Barium Salt of Paranitroorthobenzoylbenzenesulphonic Acid.

These were prepared from an aqueous solution of the barium salt by precipitating the barium exactly by means of sulphuric acid and neutralizing the free acid exactly with the carbonate of the base.

The solutions were evaporated to crystallization under a bell-jar by means of a current of dry air.

In the analyses the amount of the base is calculated on the basis of the anhydrous salt.

a. The Sodium Salt.—The sodium salt was obtained in the form of fine white crystals composed apparently of monoclinic prisms.

They appear to undergo no change on exposure to the air.

I. 0.1898 gram substance lost 0.0105 gram at 210° C., and gave 0.0384 gram Na_2SO_4.

II. 0.2022 gram substance lost 0.0111 gram at 210° C., and gave 0.0402 gram Na_2SO_4.

	Calculated for $(C_{13}H_8O_6NS)Na + H_2O$.	Found. I.	II.
H_2O	5.19	5.53	5.49
Na	6.99	6.93	6.82

b. The Potassium Salt.—The potassium salt was obtained in the form of fine white needles which were too small to indicate the form of crystallization. They became opaque on exposure to the air.

I. 0.2118 gram substance lost 0.0014 gram at 210° C., and gave 0.0546 gram K_2SO_4.

II. 0.2041 gram substance lost 0.0013 gram at 210° C., and gave 0.0518 gram K_2SO_4.

	Calculated for $(C_{13}H_8O_6NS)K$.	Found. I.	II.
K	11.33	11.63	11.46

c. The Magnesium Salt.—The magnesium salt was obtained in the form of tabular monoclinic crystals having a marked pearly luster. Some of the crystals measured nearly a centimeter in length. They appear to undergo no change on exposure to the air.

I. 0.1940 gram substance lost 0.0408 gram at 210° C., and gave 0.0294 gram $MgSO_4$.

II. 0.1997 gram substance lost 0.0425 gram at 210° C., and gave 0.0303 gram $MgSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Mg + 9\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	21.17	21.03	21.28
Mg	3.83	3.88	3.90

d. The Calcium Salt.—The calcium salt was obtained in the form of thin, pearly plates having no regular bounding planes. They become opaque on exposure to the air and crumble to a white powder.

I. 0.1373 gram substance lost 0.0096 gram at 210° C., and gave 0.0280 gram $CaSO_4$.

II. 0.1199 gram substance lost 0.0082 gram at 210° C., and gave 0.0242 gram $CaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ca + 3H_2O$.	Found. I.	II.
H_2O	7.65	6.99	6.88
Ca	6.13	6.44	6.39

e. The Lead Salt.—The lead salt was obtained in clusters of small, tabular, monoclinic crystals, which became opaque very slowly on exposure to the air.

I. 0.2121 gram substance lost 0.0219 gram at 210° C., and gave 0.0711 gram $PbSO_4$.

II. 0.2039 gram substance lost 0.0213 gram at 210° C., and gave 0.0699 gram $PbSO_4$.

III. 0.1543 gram substance lost 0.0166 gram at 210° C., and gave 0.0509 gram $PbSO_4$.

	Calculated for $(C_{13}H_9O_6NS)_2Pb + 5\frac{1}{2}H_2O$.	Found. I.	II.	III.
H_2O	10.78	10.32	10.44	10.75
Pb	25.25	25.43	25.95	25.23

The copper salt underwent decomposition on evaporation.

The Action of Phosphorus Pentachloride on the Sodium Salt of Paranitroorthobenzoylbenzenesulphonic Acid.

The sodium salt and phosphorus pentachloride in the proportion of 1 molecule to 1.5 were mixed by grinding together in an evaporating dish. There was no evidence of action, even upon adding a considerable quantity of phosphorus oxychloride, but on heating there was slight action.

The heating was continued for about ten minutes, and the pasty mass was then treated with a considerable volume of cold water. Most of the material dissolved, but a part hardened to a solid mass. After carefully washing with water this material was washed with absolute alcohol, dissolved in benzene, and crystallized out by adding an equal volume of anhydrous ether. The product separated out as clusters of small, light-colored crystals, which melted at 174°–176° C. (uncorr.) and as a scale, around the sides of the beaker, which melted at 160°–170° C. (uncorr.). It was entirely free from the dark-purple material obtained as an impurity in the preparation of paranitroorthobenzoylbenzenesulphone chloride by the action of benzene and aluminium chloride.

A considerable portion of the material was insoluble in benzene and melted at 240°–245° C. (uncorr.).

The method of formation of this material, together with its melting-point, its solubility in benzene, from which it crystallizes readily upon the addition of absolute ether, indicate that it is paranitroorthobenzoylbenzenesulphone chloride. The method of formation from the sodium salt is indicated by the following equation:

$$C_6H_3NO_2\begin{cases}COC_6H_5\\SO_2ONa\end{cases} + PCl_5 = C_6H_3NO_2\begin{cases}COC_6H_5\\SO_2Cl\end{cases} + POCl_3 + NaCl.$$

The material melting at 174°–176° C. was boiled in a flask with a return-condenser, with an excess of dilute hydrochloric

acid until it was completely dissolved. This required seven hours. The solution was filtered and evaporated to dryness on a water-bath, and the heating continued until all hydrochloric acid was driven off. The product was a dark solid, similar to that obtained by the action of acid on paranitroorthobenzoylbenzenesulphone chloride. An excess of barium carbonate was added to an aqueous solution of the product, the excess of carbonate filtered off, and the solution, which had the characteristic bitter taste of the barium salt of paranitroorthobenzoylbenzenesulphonic acid, evaporated under a bell-jar. On evaporation the solution yielded a small amount of a crystalline barium salt.

The formation of paranitroorthobenzoylbenzenesulphonic acid by the action of hydrochloric acid on the product of the action of phosphorus pentachloride on the sodium salt of paranitroorthobenzoylbenzenesulphonic acid, and its conversion into the barium salt confirms the view already expressed that the action of phosphorus pentachloride on the sodium salt gives the sulphone chloride.

The Action of Concentrated Ammonia on Paranitroorthobenzoylbenzenesulphone Chloride.

As the result of several experiments it was found that, by heating the chloride in a sealed tube for two or two and a half hours in a water-bath, it is mainly converted into a clear, granular product, which melts at 234° C. (uncorr.).

A small amount of a dark, high-melting product is also formed as a thin coating, and can easily be removed mechanically or dissolved in alcohol, which dissolves it readily without dissolving the main product.

The material thus prepared is obtained in the form of a light-green, granular powder, having a constant melting-point of 234° C. (uncorr.). The substance contains no chlorine.

I. 0.2014 gram substance gave 15.81 cc. N.
II. 0.1970 gram substance gave 15.67 cc. N.
III. 0.2075 gram substance gave 0.1756 gram $BaSO_4$.
IV. 0.2011 gram substance gave 0.1692 gram $BaSO_4$.

	Calculated for $C_6H_3NO_2\langle^{C(C_6H_5)}_{SO_2}\rangle N$.	Found. I.	Found. II.
N	9.72	9.86	9.99
S	11.11	11.60	11.55

The results of analysis, together with those described in the following section, indicate that the main product of the action of concentrated ammonia on the chloride is the lactim of paranitroorthobenzoylbenzenesulphonic acid. The reaction by which it is formed is represented as follows:

$$C_6H_3NO_2\langle^{COC_6H_5}_{SO_2Cl} + NH_4OH = C_6H_3NO_2\langle^{C(C_6H_5)}_{SO_2}\rangle N + HCl + 2H_2O.$$

The lactim is insoluble in water, only slightly soluble in alcohol and readily soluble in benzene.

The formation of the lactim of the sulphonic acid by the action of concentrated ammonia agrees with the formation of the lactim of orthobenzoylbenzenesulphonic acid by the action of dry ammonia gas on the sulphone chloride as observed by Remsen and Saunders.[1]

The Action of Concentrated Ammonia on the Lactim of Paranitroorthobenzoylbenzenesulphonic Acid.

The presence of a red-colored, amorphous product, melting above 275° C. (uncorr.), with the lactim formed by the action of ammonia on the chloride, together with the fact that the amount of this product was increased as the length of time of heating was increased, indicated that another product was formed by the continued action of ammonia. A considerable quantity of this material was prepared by heating some of the paranitroorthobenzoylbenzenesulphone chloride in a sealed tube until the only product consisted of the red-colored substance desired. It was found necessary to heat it to the temperature of the water-bath for twenty-four hours in order to effect this transformation, while two and a half hours were sufficient to transform the sulphone chloride into the lactim.

[1] *Loc. cit.*

The product is insoluble in water, but dissolves readily in absolute alcohol, giving a red solution with a marked green fluorescence. It is thrown out of solution by adding a considerable volume of water.

On evaporating the alcoholic solution it is deposited as a red-colored crust which seems to possess no crystalline structure.

0.2150 gram gave 19.24 cc. N = 11.24 per cent N.

0.1615 gram gave 0.1200 gram $BaSO_4$ = 10.20 per cent S.

The results of the analysis show that while the percentage of sulphur remains about the same as in the lactim, the percentage of nitrogen is increased, but not to an amount corresponding to the composition of any substance likely to be derived from the lactim by the further action of ammonia.

These results, together with the impossibility of obtaining the product in crystalline condition and its properties generally indicate that it is probably not a definite chemical compound, and that the lactim probably undergoes decomposition by the further action of ammonia.

The Action of Dilute Hydrochloric Acid on the Lactim of Paranitroorthobenzoylbenzenesulphonic Acid.

The action of hydrochloric acid on the lactim was first tried by boiling in a flask, provided with a return-condenser, with an excess of acid. The lactim showed but little change after boiling with the acid for thirty hours. The acid was colored yellow, but this was found to be due to solution of the lactim. By evaporating off the acid, the lactim is recovered with its melting-point unchanged.

By heating the lactim with a large excess of hydrochloric acid in a closed tube to 150°–175° C. in a furnace for five hours, about half of the lactim is dissolved and is not deposited on cooling. On heating to 200° C. for seven hours longer, all of the lactim goes into solution, and is not deposited on cooling, and the acid has a dark-yellow color. On evaporating the filtered acid solution, a yellow, crystalline product is obtained, which has not a constant melting-point. The melting-point, immediately after pressing out between filter-paper, is 100°–160° C. (uncorr.), and it is charred by heating to 210°

C. (uncorr.) in an air-bath. If, however, it is first carefully dried, it appears to melt at a much higher temperature.

This indicates that the product is a salt which melts in its water of crystallization.

Analysis of a sample carefully dried:

0.2009 gram gave 14.33 cc. N.

0.1692 gram gave 0.1264 gram $BaSO_4$.

	Calculated for $C_6H_3NO_2\langle^{COC_6H_5}_{SO_3ONH_4}$	Found.
N	8.64	8.95
S	9.88	10.24

The results of analysis indicate that the product is the ammonium salt of paranitroorthobenzoylbenzenesulphonic acid. The transformation takes place according to the following equation:

$$C_6H_3NO_2\langle^{C}_{SO_2}\rangle\!\!>\!\!N^{C_6H_4} + 2H_2O = C_6H_3NO_2\langle^{COC_6H_5}_{SO_3ONH_4}.$$

The ammonium salt thus obtained has generally the form of a yellow crystalline powder, but under the conditions existing in one of the experiments, a few thick, needle-shaped crystals about a centimeter long were obtained. It dissolves readily in water.

Summary.

The principal results obtained in the foregoing investigation may be briefly stated as follows:

By using phosphorus pentachloride in the proportion of 2.5 molecules to 1 of the anhydrous acid potassium salt and heating for five hours under the conditions indicated, the unsymmetrical chloride is the only product.

This may be crystallized readily at the temperature of the laboratory by using ligroin (90°–125°) as the solvent, provided the impurities are first removed by washing with ligroin (50°–80°).

The action of benzene and aluminium chloride on the symmetrical and on the unsymmetrical chloride gives, in both cases, paranitroorthobenzoylbenzenesulphone chloride.

The action of hydrochloric acid, concentrated or dilute, dilute sulphuric acid, water, and alcohol on paranitroorthobenzoylbenzenesulphone chloride is the same. The product formed is, in each case, paranitroorthobenzoylbenzenesulphonic acid.

The action of phosphorus pentachloride on the sodium salt of paranitroorthobenzoylbenzenesulphonic acid gives rise to the formation of paranitroorthobenzoylbenzenesulphone chloride identical with that from which the acid was derived by the action of acids or water.

The action of concentrated ammonia on paranitroorthobenzoylbenzenesulphone chloride for a limited length of time gives the lactim of paranitroorthobenzoylbenzenesulphonic acid.

The further action of concentrated ammonia gives a substance of indefinite composition, which probably indicates a decomposition of the lactim first formed.

The continued action of concentrated hydrochloric acid at a high temperature in a sealed tube converts the lactim into the ammonium salt of paranitroorthobenzoylbenzenesulphonic acid.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

STEREOISOMERS AND RACEMIC COMPOUNDS.

BY HERMAN C. COOPER.

I. Solubility of Stereoisomers in an Indifferent Active Solvent.

The possibility of a difference in solubility of two optical isomers in an active solvent has been recognized ever since the researches of Pasteur.[1] In a recent paper[2] the writer, together with Heinrich Goldschmidt, who first directed his attention to the matter, presented experimental evidence indicating that the two optically active carvoximes have the same solubility in *d*-limonene. Tolloczko[3] had by a different method previously come to similar conclusions in the cases of the tartaric acids in amyl alcohol and the mandelic acids in

[1] Ann. chim. phys. [3], **38**, 437; Cf. also Van 't Hoff-Eiloart, Atoms in Space, 1898, p. 45.

[2] Ztschr. phys. Chem., **26**, 711.

[3] *Ibid.*, **20**, 412.

levulose solution. Kipping and Pope,[1] however, announce that, on allowing a racemic mixture to crystallize from an optically active solution, the first fractions show a preponderance of crystals of one of the isomers. Thus, the first crystallization of sodium ammonium racemate from aqueous dextrose solution at a temperature below the transition-point was found to consist chiefly of dextrotartrate. As this seems to suggest a difference of solubility of the two active tartrates in dextrose solution, it appeared desirable to use the same simple method employed in the carvoxime-limonene test[2] to obtain more light on this matter.

On account of the rather large solubility of the sodium ammonium tartrates in water and their tendency to weather, the stable sodium hydrotartrates were first examined. In the light of the present structural theory of optical isomers it is very unlikely that the addition of an NH_4 group each to both isomers would alter their relative behavior towards an active solvent. The probability of electrolytic dissociation of tartrates in such a solution renders this all the less likely.

Sodium Hydrotartrates in Aqueous Dextrose Solution.—The dextrotartrate was prepared by mixing the theoretical amounts of sodium carbonate and ordinary c. p. tartaric acid in water; the laevo salt in a similar manner from *l*-tartaric acid obtained by the Pasteur-Anschütz crystallization method.[3] After recrystallization the salts were tested as to rotatory

[1] Proc. Chem. Soc., 1898, 113.

[2] Goldschmidt and Cooper: *Loc. cit.*

[3] A careful comparison of the three well-known Pasteur methods has shown the crystallization process to be the most reliable in securing a satisfactory yield about whose rotatory power no anxiety need be felt. By the improved cinchonine method (Ber. d. chem. Ges., **29**, 42) much time is consumed in the recovery and purification of the racemic acid and cinchonine unless one is working on a large scale, while with a little care a concentrated solution of Scacchi salt can after a short period in a cold room be made to yield homogeneous crystals of 1–5 grams each. The first one that can be crystallographically identified as laevo should be used to prepare a calcium-tartrate solution, and the neat Anschütz test (Ann. Chem. (Liebig), **226**, 193) at once applied to all the other crystals. If the sample is taken from different parts of the crystals, the ones so recognized as laevo will be found, after recrystallization from 60 per cent alcohol, to furnish a tartrate of unquestioned purity, from which the laevo acid is easily obtained by treatment with lead acetate and hydrogen sulphide.

Sowing the original solution with laevo crystals is of advantage for the first one or two crops but supersaturation with reference to the dextrotartrate soon becomes so great that laevo crystals are dissolved while dextro crystals are formed. For this reason it is better to sow dextro and laevo crystals simultaneously at different places in the solution.

power with a thoroughly reliable Laurent half-shadow polarimeter.

1. *d*-$NaC_4H_5O_6 + H_2O$. 1.5350 grams dissolved in water to 25 cc.; $c = 6.1400$; $t = 21°$; $l = 2dm$; $\alpha = +2°42'.3$; $[\alpha]_D^{21} = +22°.03$.

2. *l*-$NaC_4H_5O_6 + H_2O$. 1.5350 grams dissolved in water to 25 cc.; $c = 6.1400$; $t = 19°.5$; $l = 2dm$; $\alpha = -2°42'$; $[\alpha]_D^{19.5} = -21°.98$.

A comparison of these figures with the table of Thomsen[1] shows that the substances may be considered perfectly pure. The dextrose solution used possessed a density of 1.14, a strength of 32.5 per cent, and a rotatory power of $[\alpha]_D^{20} = 53°.8$.

Weighed quantities of tartrate and dextrose solution were sealed up in small glass tubes and the temperature determined at which complete solution took place.[2] By working with a No. 20 beaker-glass and carefully avoiding disturbing air currents the temperature could easily be held constant to 0°.1 below 50°, and to at least 0°.2 between 50° and 70°. The tubes were allowed to rotate about 60–70 times a minute. In cases where the concentration, and consequently the solution-temperature, was high the question as to just when complete solution took place was decided by removing the tube and allowing it to remain several hours at room temperature. If all solid particles had disappeared, supersaturation resulted and no separation of solid matter followed; otherwise the tube was replaced and the test continued. A table of results follows:

d-Tartrate in Dextrose Solution.

Gram tartrate.	Grams dextrose solution.	Grams tartrate to 100 grams dextrose solution.	Solution temperature.
0.1782	2.3202	7.68	32°.9
0.1984	1.8949	10.47	43°.6+
0.1946	1.1200	17.38	61°.6

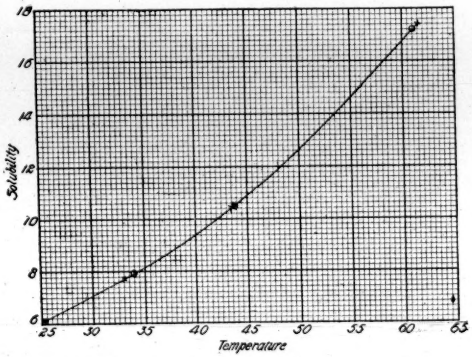
[1] J. prakt. Chem. [2], **31**, 85.

[2] For description of apparatus see Ztschr. phys. Chem., **26**, 713; and also Fig. 125, Ostwald-Walker's Physico-chem. Measurements (1894).

l-Tartrate in Dextrose Solution.

0.1756	2.8700	6.12	25°.2
0.2006	2.5330	7.92	34°.0
0.1998	1.9066	10.48	43°.7
0.1943	1.1301	17.19	61°.1

The parallelism of the results in the two cases is better shown by plotting them as curves. Let the figures in the third column, representing solubility, be the ordinates and those in the fourth column, representing the corresponding temperatures, be the abscissae. The crosses indicate *d*-tartrate, the circles *l*-tartrate.



As a further check on the results we may apply the solubility formula, $S = a + bt + ct^2$, which, using the values at 25°.2, 34°.0, and 43°.7, becomes $S = 3.72 + 0.01443t + 0.003211t^2$ for dextrotartrate. Interpolating for 32°.9 we have $S = 7.67$. 7.68 was found experimentally for *l*-tartrate. It is plain that there is no justification for the assumption of two separate curves and we must conclude that there is no difference in solubility.

Sodium Ammonium Tartrates in Aqueous Dextrose Solution.—A few experiments were then similarly made with the sodium ammonium tartrates. Each of these salts was recrystallized from 60 per cent alcohol, the solution being agita-

ted to produce small crystals, and the resulting crystals were washed with alcohol and dried first on filter-paper and then a few minutes in a vacuum desiccator. In each experiment nearly equal proportions of dextro and laevo salt were used and the two tests carried out simultaneously (temp. as under I). After subsequent cooling each experiment was repeated (II).

Exp. I.—Material obtained from Neutralizing the Previously Prepared Hydrotartrates with Ammonia.

	Gram $NaNH_4C_4H_4O_6 + 4H_2O$.	Grams dextrose sol.	Grams tartrate to 100 grams dextrose sol.	Solution temperature. I.	II.
Dextro	0.6668	1.0846	6.15	27°.3	27°.4
Laevo	0.6682	1.0870	6.14	27°.6	27°.6+

Exp. II.—Material from Freshly Separated Tartrates.

Dextro	0.5222	1.0652	4.90	22°.1	21°.9
Laevo	0.5300	1.0733	4.94	21°.8	21°.9

Exp. III.—Material as in Exp. II.

Dextro	0.4918	0.9886	4.97	22°.2	22°.2
Laevo	0.4920	0.9891	4.97	22°.15	22°.2

The slight variation in the results seems to be due to the rather large experimental error, anticipated above, and we are hardly justified in assuming any considerable difference in solubility. It is therefore very probable that a solution of an externally compensated mixture of the sodium ammonium tartrates, in a concentration strong enough to cause crystallization, will in time yield practically equal quantities of the two modifications. Nevertheless, if the dextrose molecules exert even the slightest influence, so that the first crystal molecule formed is dextro, that individual will have the same effect on the crystallization as the introduction of a dextro crystal. No intrusion on the field of Messrs. Kipping and Pope is planned, but it is to be hoped that they will ascertain whether a laevo-rotatory solvent has the opposite effect from that of dextrose solution.

II. Properties of Inactive Mixtures.

Melting-point.—The following data supplement the inter-

esting work of Centnerszwer.[1] Sodium hydrotartrate decomposes at 234°, a point sharply indicated by a sudden rise of substance in the m. p. tube. The racemate decomposes at 219°, and a mixture of approximately equal parts of the optical isomers at 222°.

A mixture of approximately equal parts of the active carvoximes was found to melt at the same temperature as inactive carvoxime; *viz.*, 93°. A slight shrinking was to be observed at 72°, the melting-point of the active body.

Solubility.—On mixing equal amounts of the active sodium hydrotartrates in water, a cloudy precipitate of racemate appears and does not disappear till the temperature of the solution of the racemate is reached. A similar mixture of the active carvoximes in aqueous alcohol gives no precipitate of racemic compound, but, nevertheless, has the same solubility as an amount of racemic carvoxime equal to the weight of the mixture.

III. Partial Racemism.

The credit of having established the existence of partial racemic compounds must be ascribed to Ladenburg, who identified racemic quinine pyrotartrate[2] as the first example. Other examples have been subsequently announced by Ladenburg and Doctor,[3] and by Pope and Peachey.[4] It will be noticed that there is no essential difference between them, each being made up of two components which possess the same chemical composition, differing only as $+A+B$ and $+A-B$ or $+A+B$ and $-A+B$, in which A represents an acid, B a basic radical. Is it not possible, however, for a racemic compound to exist whose active components are not chemically equivalent? When one considers the facility with which some optical isomers unite to form racemic compounds of distinctly different physical properties, the question easily arises whether a slight modification of one isomer, such as substitution in a position remote from the asymmetric carbon atom, necessarily renders racemic association impossible.

[1] Ztschr. phys. Chem., **29**, 715.
[2] Ber. d. chem. Ges., **31**, 524, 937.
[3] *Ibid.*, **31**, 1969.
[4] Ztschr. Kryst. u. Min., **31**, 11.

Such a case, if discovered, would certainly broaden our ideas of racemic bodies. Reasoning somewhat in this way, Küster[1] has suggested the possibility of chlorbenzoyl-*d*-tartrate and brombenzoyl-*l*-tartrate uniting to form a partial racemate.

In Pasteur's notable monograph[2] entitled "Nouvelles Recherches," ammonium bimalate is said to form a definite compound with dextroammonium bitartrate, not, however, with laevoammonium bitartrate. This discovery of a half century ago has apparently been frequently overlooked, no mention of it being found in Bischoff-Walden's "Stereochemie" or Van 't Hoff-Eiloart's "Arrangement." The compound was found to consist of 1 molecule of *d*-ammonium bitartrate and 1 molecule of *l*-ammonium bimalate. Inasmuch as the atomic difference between the two molecules is very slight, it seems quite likely that we have here to deal with a case of partial racemism as above suggested. A repetition and extension of Pasteur's experiments is planned, covering all the tartro-malic compounds, and the much discussed "criteria" of racemic compounds will be carefully applied. Some preliminary experiments with sodium bitartrate and sodium bimalate have disclosed interesting relations.

OBITUARY.

CARL FRIEDRICH RAMMELSBERG.

The long and useful life of Carl Friedrich Rammelsberg ended on December 28th of the past year. He was born in Berlin, April 1st, 1813, and after a thorough school training spent five years as an apothecary. He then matriculated at the university and devoted himself to physics, chemistry, mineralogy, and botany under the most distinguished teachers of that day, working in the laboratory of Mitscherlich. Later he established the first laboratory specially devoted to the instruction of students in inorganic analysis. He became in succession privatdocent, extraordinary, and ordinary professor in the University. Meantime his marvelous industry showed itself in the publication of numerous papers on mineral chemistry, the number of these alone amounting to more than 150. He made also valuable investigations in many branches

[1] Ber. d. chem. Ges., **31**, 1853.
[2] Ann. chim. phys. [3], **38**, 460.

of pure inorganic chemistry, and as an excellent crystallographer did much to further the study of crystalline form as an essential part of descriptive chemistry. The list of his special treatises, handbooks, and introductions is a long one and many of them even now have a real value as works of reference and well illustrate the broad view which he took of his own favorite branches of science. He was able to pursue his laboratory work long after the age when most chemists are obliged to content themselves with only looking on at the progress of their science. Personally he was much beloved by his pupils and was conscientious as a teacher as well as an investigator. The writer of this brief notice, as one of Rammelsberg's pupils, offers these words of appreciation of the man and of his work. W. G.

NOTES.

Polonium and Radium.

Some years ago Becquerel, while working with uranium and some of its salts, found that certain of the salts, although they are not fluorescent, nevertheless have the power of emitting rays which are different from the Roentgen rays. These new rays have the power of rendering gases through which they pass conductors of electricity and of producing impressions on photographic plates. They are also capable of being transmitted through opaque bodies, but suffer greater absorption than the Roentgen rays.

Shortly after Becquerel's work, Schmidt found that thorium and its salts emit the same kind of rays as uranium and its salts, but that the former are less intense than the latter.

While investigating pitchblende and other minerals closely allied to it, which contain uranium and thorium, M. and Mme Curie[1] discovered the new substance which they called polonium, after the native country of Mme. Curie. They called the property of emitting Becquerel rays "radioactivity", and found that the sample of pitchblende with which they were working was two or three times as radioactive as uranium. Since the salts of uranium are less active than metallic uranium, they concluded that the great radioactivity of pitchblende is due to the presence of a small amount of some strongly radioactive substance. They passed hydrogen sulphide into an acid solution of the pitchblende. The uranium and thorium remained in solution, and besides lead, bismuth, copper, arsenic, and antimony, a very active substance was pre-

[1] Compt. rend., **127**, 175 (1898); Chem. News, **78**, 40 (1898).

cipitated. The active sulphide is insoluble in ammonium sulphide, which separated it from arsenic and antimony. The sulphides insoluble in ammonium sulphide were dissolved in nitric acid, and the lead precipitated with sulphuric acid. Some of the active substance is carried down with the lead, and can be covered by treating the lead sulphate with dilute sulphuric acid, which dissolves the active substance. There were then in solution the active substance, bismuth and copper. Ammonia precipitated the first two completely, thus separating them from the copper. It was impossible to separate the active substance from bismuth in the wet way. On dissolving them both in nitric acid and adding water, it was found that the portions first precipitated are by far the most active. Further, when the mixed sulphides from pitchblende are heated in a vacuum in a glass tube to about 700°, the active substance sublimes in the portion of the tube heated to 250°–300°, while the bismuth remains in the warmer part of the tube. By these methods the investigators obtained a substance which was 400 times as active as uranium. Specimens of it were sent to Demarçay to be examined spectroscopically, but his results were unsatisfactory.

While working on polonium M. and Mme. Curie[1] discovered a second new radioactive substance, closely allied to barium and different from polonium, which they called radium. This new radioactive substance is obtained from pitchblende together with barium, and it has not been possible to separate it from barium. It is not precipitated by hydrogen sulphide, ammonium sulphide, nor ammonia; its sulphate is insoluble in water and acids; its carbonate is insoluble in water; the chloride is very soluble in water, but insoluble in concentrated hydrochloric acid and in alcohol. The substance, as first obtained by its discoverers, was in the form of the chloride and then had a radioactivity 60 times as great as that of uranium. On dissolving the chloride in water and precipitating with alcohol, the portions first precipitated are the most active. In this way a substance was finally obtained which was 17000 times as radioactive as uranium. Demarçay[2] examined the spectrum of this substance and found in it the barium lines, the platinum lines due to the electrodes, the calcium and lead lines, which were very weak, probably due to impurities, and a series of new lines which were fully as intense as the barium lines, and which could not possibly belong to any of the known elements. The new lines in the spectrum were comprised between $\lambda = 4826.3$

[1] Compt. rend., **127**, 1215 (1898); Chem. News, **79**, 1 (1899).

[2] Compt. rend., **127**, 1218 (1898); *Ibid.*, **129**, 716 (1899); Chem. News, **29**, 13 (1899); *Ibid.*, **80**, 269 (1899).

and $\lambda = 3649.6$. The strongest new line, which was as strong as the strongest barium line, had $\lambda = 3814.7$. The results of the spectroscopic examination, together with the fact that barium and its compounds are not in the least radioactive, led M. and Mme. Curie to the conclusion that they had a new substance to deal with.

The atomic weight[1] of the metal contained in some of the most active specimens of radiferous barium chloride was determined with the following results:

a.	*M.*	*Ba.*
3000	140.0	138.1
4700	140.9	137.6
7500	145.8	137.8

a represents the activity of the chloride, the activity of uranium being taken as 1, *M* represents the atomic weight of the metal in the radiferous chloride, and *Ba* represents the atomic weight of barium from pure, inactive barium chloride, whose atomic weight was determined each time that the metal in the radiferous chloride was determined. The atomic weights were determined by estimating the amount of chlorine in the anhydrous chlorides with silver nitrate.

Becquerel rays and the rays from polonium and radium seem to be essentially the same in character, but they differ in intensity. The rays from radium are the strongest, those from thorium the weakest. The radium rays will produce an impression on a photographic plate in half a minute, while under the same conditions the uranium rays require an hour to produce the same impression. Rays from polonium and radium excite fluorescence in barium platinocyanide, weaker to be sure than that caused by Roentgen rays, but uranium and thorium rays excite no fluorescence at all on account of their weaker radioactivity. Radioactive substances also have the power of inducing radioactivity in inactive substances, and this induced radioactivity continues for several days after the originally radioactive substance has been removed. In this respect Becquerel rays differ markedly from Roentgen rays which produce a secondary effect in bodies only as long as the rays strike such bodies.

Becquerel rays seem to have the power of inducing chemical action.[2] It was observed that when bottles containing radiferous barium chloride were opened, the odor of ozone was very perceptible. This odor was dissipated after the bottle had stood open for some minutes, but was noticeable again when the bottle was opened after having been closed for

[1] Compt. rend., **129**, 760 (1899); Chem. News, **80**, 281 (1899).

[2] Compt. rend., **129**, 1823 (1899).

some time. Also, the glass of bottles in which the chloride is kept assumes a violet color where it comes in contact with the salt. Villard[1] noticed a similar effect when glass is subjected to the action of Roentgen rays, while at the same time it is protected from the cathode rays. It is concluded that this coloration of the glass is due to the oxidation of manganese which is contained in it. Further, the action of Becquerel rays on barium platinocyanide seems to be of a chemical nature. The salt under the effect of these rays becomes fluorescent and turns yellow. It then loses its fluorescence and becomes dark-brown. If now it is exposed to the sunlight, it again acquires the property of becoming fluorescent when struck by Becquerel rays.

To account for the continuous disengagement of energy from radiferous bodies, several views have been advanced. It might be due to a phosphorescence of very long duration, caused by the action of light, or it might be due to an emission of matter accompanied by a loss of weight of the radiferous bodies. Again, it might be a secondary emission provoked by rays which are constantly in existence in space and which are absorbed only by certain elements.

Quite recently, M. Debierne[2] has obtained another radioactive substance from pitchblende, which is closely allied to titanium in its chemical properties. It differs from radium in that it is not luminous in the dark, while radium is luminous. C. E. C.

Asymmetric Optically Active Nitrogen Compounds.

Messrs. Pope and Peachey[3] have recently published an interesting article on the above subject. From this the following extracts are taken:

"The only direct evidence pointing to the existence of asymmetrically optically active nitrogen compounds is Le Bel's observation[4] that on cultivating *Penicillium glaucum* in solutions of isobutylpropylethylmethylammonium chloride the liquid acquires a rotatory power of —0°25′ or —0°30′ under favorable conditions. The value of this important observation is, however, considerably lessened by the fugitive nature of the optical activity and by the failure of Marckwald and von Droste-Huelshoff[5] to confirm Le Bel's results. (Le Bel has recently replied to Marckwald and von Droste-Huelshoff's criticism,[6] and has confirmed his previous results.)

[1] Compt. rend., **129**, 882 (1899).
[2] *Ibid.*, **129**, 593 (1899).
[3] J. Chem. Soc., December, 1899.
[4] Compt. rend., 1891, **112**, 724.
[5] Ber. d. chem. Ges., **32**, 560.
[6] Compt. rend., **129**, 548.

"Many futile attempts have been made to directly resolve quaternary bases of the type $N(OH)X_1X_2X_3X_4$ into optically active antipodes by means of optically active acids. Thus Marckwald and von Droste-Huelshoff[1] attempted to resolve Le Bel's base by the aid of tartaric, camphoric, and mandelic acids, whilst Wedekind[2] endeavored to resolve α-benzoylphenylallylmethylammonium hydroxide by means of tartaric and camphoric acids; in no case, however, was an optically active base obtained.

"A consideration of the facts led to the opinion that the failure of these and other attempts had its origin in the facility with which tetralkylammonium salts are decomposed by water and converted into tertiary base and alcohol; we, therefore, prepared α-benzylphenylallylmethylammonium iodide by Wedekind's[3] method and were successful in resolving it into isomeric optically active bases by using hydroxyl-free solvents containing only small quantities of water. A number of methods, differing in detail, were applied, but we ultimately adopted the following process as affording the best results:

"Carefully purified α-benzylphenylallylmethylammonium iodide was mixed with a molecular proportion of the anhydrous silver salt of Reychler's dextrocamphorsulphonic acid and boiled for an hour or so on the water-bath with a mixture of about equal parts of acetone and, ethylic acetate, a few drops of water being added when necessary. After separating silver iodide from the gummy solution by filtration the solvent was distilled off, and, on cooling, the residue solidified to a crystalline mass consisting of a mixture of dextro- and laevobenzylphenylallylmethylammonium dextrocamphorsulphonate.

"By fractionally crystallizing the mixture of dextrosulphonates from boiling acetone the less soluble constituent, dextro-α-benzylphenylallylmethylammonium dextrocamphorsulphonate, was readily obtained in colorless, diamond-shaped plates melting at 169°–170°."

The authors show that the molecular rotatory power of the basic radical of this salt is +150°.

The corresponding laevo salt was obtained from the acetone mother-liquors, and this was found to have a marked laevo rotatory power.

From the two dextrosulphonates the corresponding iodides and bromides were obtained.

In concluding their article the authors say:

"In the present paper it is proved that quaternary ammo-

[1] *Loc. cit.*
[2] Ber. d. chem. Ges., **32**, 517.
[3] *Loc. cit.*

nium derivatives in which the five substituting groups are different, contain an asymmetric nitrogen atom which gives rise to antipodal relationships of the same kind as those correlated with an asymmetric carbon atom. The method which has enabled us to deal with quaternary bases is now being applied to various other types of substituted ammonium derivatives in order to ascertain the stereochemical nature of pentad nitrogen. We hope shortly to be in a position to publish results obtained with sulphonium derivatives of the type $SX_1X_2X_3I$." I. R.

REVIEWS.

LES SUCRES ET LEURS PRINCIPAUX DÉRIVÉS. Par L. MAQUENNE, Professeur au Muséum d' Histoire Naturelle. Paris: Georges Carré et C. Naud, éditeurs. 1900. 1032 pp.

The author of this handbook has done chemists a service by compiling from the great mass of papers appearing within the last few years on the sugars and closely allied substances—largely due to the labors of E. Fischer and his pupils and coworkers—a general *résumé* of our present knowledge in the field in question. Not only are the general principles of stereoisomeric chemistry applied systematically to the classification and nomenclature of the sugars, but the preparation and properties of the now numerous substances of this class are described with a very fair degree of detail, considering the moderate size of the book, and its value is greatly enhanced for the practical worker by copious references to the original papers which have been collated, French, Russian, and other sources being drawn upon as well as German. The transformations by hydrolysis, fermentation, etc., are gone into in brief but intelligible fashion, connecting the sugars with each other and with their chief derivatives of other classes, and methods of determination for the principal sugars are discussed in their practical bearings. The notice taken of some allied substances, such as starch and cellulose, seems to be hardly in proportion to the work upon them which has been done in recent years, though there are references to the more important memoirs. In agreeable contrast with the usage of most French writers, the author has appended a convenient index, as well as the usual table of contents. J. W. M.

MODES OPÉRATOIRES DES ESSAIS DU COMMERCE ET DE L'INDUSTRIE. Par L. CUNIASSE et R. ZWILLING, Chimistes-Experts de la Ville de Paris. Paris: Georges Carré et C. Naud, éditeurs. 1900. 302 pp.

In the preface to this little book, by M. Ch. Girard, it is suggested that it is intended for the use of young men who

expect to enter industrial laboratories, and is to occupy an intermediate place between the large treatises for professional men and the small text-books for beginners. There is included much good matter, in general clearly presented and in highly condensed form, but condensation has been carried so far that, for many of the topics treated of, the work can hardly be considered as more than an index, and must prove of small value in the absence of larger handbooks. Thus, the whole subject of iron is disposed of in about three and a half small pages (no notice is taken of steel), glass in a page and a quarter, fuel in less than three pages, soap in a little more than three pages, and butter in about a page. Some other subjects have more space devoted to them, as, for example, there are ten and a half pages on milk, fifteen pages on sugar, and nearly twenty pages on wine. A few materials are included which are not commonly found in the smaller manuals of this kind, such as wood- and coal-tar creosote, vulcanized india-rubber, and gutta percha. J. W. M.

WATER AND WATER SUPPLIES. By JOHN C. THRESH, D.Sc. (London). Philadelphia: P. Blakiston's Son & Co. (printed in England). 1900. 431 pp.

A generally well-compiled and well-balanced summary of the most important facts—geological, chemical, bacteriological, and engineering—bearing upon natural water as obtainable for human use. In regard to most of the questions which have given rise to difference of opinion the author seems to fairly, and without partisanship, sum up the present state of our knowledge, as, for instance, in the chapters on the interpretation of water analyses and the so-called self-purification of rivers. The book is written essentially from an English point of view, and would be increased in value if more extended notice were taken of the investigations made and results obtained in other countries. The three subjects which receive distinctly inadequate notice are: the effects of various kinds of natural waters upon metallic pipes and iron or steel boilers; the relations of natural waters to special manufacturing uses, such as brewing, dyeing, and paper-making, and the effects on streams of special manufacturing refuse; and the rapid mechanical filtration of water on the great scale, aided by coagulants, as now largely practiced in the United States. J. W. M.

OUTLINES OF INDUSTRIAL CHEMISTRY. By FRANK HALL THORP, PH.D., Instructor in Industrial Chemistry in the Massachusetts Institute of Technology. New York: The Macmillan Company. New edition, revised. 1899. 541 pp.

The appearance of a second edition of this work a year after

its first publication is a favorable indication of its having proved acceptable. As the author says in his new preface that he has limited himself to the correction of errors which have been noticed, and has made no material change in the text, there seems to be occasion for little more than a repetition of the remarks made in a former notice in this JOURNAL (Vol. **21**, p. 181). It is to be hoped that the press of other work referred to as the reason for not extending or recasting any parts of the book may not long prevent the bringing out an edition with such changes and improvements, particularly in regard to the illustrations, as might easily develop the work into a very useful manual for students. J. W. M.

INTRODUCTION TO PHYSICAL CHEMISTRY. By JAMES WALKER., D.Sc., PH.D., Professor of Chemistry in University College, Dundee. New York and London: Macmillan & Co. 1899. 335 pp.

This work does not aim to be a systematic text-book covering the whole field of physical chemistry, but treats certain chapters at considerable length. Dr. Walker states the purpose which he had in mind in writing this book, as follows: "I have found in the course of ten years' experience in teaching the subject, that the average student derives little real benefit from reading the larger works which have hitherto been at his disposal, owing chiefly to his inability to effect a connection between the ordinary chemical knowledge he possesses and the new material placed before him. He keeps his every-day chemistry and his physical chemistry strictly apart, with the result that instead of obtaining any help from the new discipline in the comprehension of his systematic or practical work, he merely finds himself cumbered with an additional burden on the memory, which is to all intents and purposes utterly useless. This state of affairs I have endeavored to remedy in the present volume."

Some of the subjects treated are: The Atomic Theory and Atomic Weights; The Simple Gas Laws; The Periodic Law; Solubility; Fusion and Solidification; Vaporization and Condensation; The Kinetic Theory and van der Waals' Equation; The Phase Rule; Relation of Physical Properties to Composition and Constitution; The Properties of Dissolved Substances; Osmotic Pressure and the Gas Laws for Dilute Solutions; Methods of Molecular Weight Determination; Electrolysis and Electrolytes; Electrolytic Dissociation; Balanced Actions; Rate of Chemical Transformation; Relative Strengths of Acids and Bases; Applications of the Dissociation Theory; Thermodynamical Proofs.

The chapter on the Phase Rule is by far the clearest and most concise treatment of this subject which has thus far appeared.

Under methods for determining molecular weights, in addition to those ordinarily employed for vapors and solutions, we find a brief account of the beautiful method of Ramsay and Shields, by which the molecular weight of pure liquids can be determined by measuring their surface-tension. It is unfortunate that this method is too delicate for general laboratory use, since much of importance would undoubtedly be brought to light by its further application.

It seems a little out of keeping with the remainder of the work, that the very defective method of Nernst and Loeb should be recommended for determining the relative velocities of ions, now that we have methods which are so much more refined.

The work, as a whole, is admirably written in a clear and attractive style and can be heartily recommended to any one who is beginning the study of physical chemistry.

H. C. J.

A TEXT-BOOK OF PHYSICAL CHEMISTRY. By DR. R. A. LEHFELDT, Professor of Physics at the East London Technical College. London: Edward Arnold. 1899 308 pp.

The author points out what is generally recognized, that the new physical chemistry has not been accorded the hearty welcome in England which it deserves. "It is time, too, to appeal for wider recognition in England, where, as yet, not a single professorship exists to mark the appearance of a new science that on the continent has long been regarded as wide enough to require a man's whole energy." A brief quotation from the preface will show what is the aim of this little book: "The present book is intended to contain what a student—with limited time and many subjects to learn—may usefully read. * * The author hopes that the style adopted will put the reader, as far as possible, in touch with the constant stream of experimental and theoretical research that makes physical chemistry at present such a fascinating subject to follow."

The subject is dealt with in seven chapters: Determination of Molecular Weight; Physical Constants in Relation to Chemical Constitution; The Principles of Thermodynamics; Chemical Dynamics of Homogeneous Systems; Chemical Dynamics of Heterogeneous Systems; Application of Thermodynamics to Chemical Equilibrium; Electrochemistry.

The work is clearly written and is quite up to date. The abbreviation *Ostw.* for Zeitschrift für physikalische Chemie, is not customary, and is a little perplexing until one consults the list of abbreviations, since we should naturally think that this referred to Ostwald's Lehrbuch. But this is of little con-

sequence. The book will doubtless contribute much to the advancement of physical chemistry wherever it is used.

H. C. J.

OPTICAL ACTIVITY AND CHEMICAL COMPOSITION. By DR. H. LANDOLT, Professor of Chemistry in the University of Berlin. Translated with the author's permission by JOHN MCCRAE, PH.D. London and New York: Whittaker & Co. 1899. 158 pp. Price, $1.00.

This is a translation of the eighth chapter of the first volume of Graham-Otto's "Lehrbuch der Chemie." Professor Landolt is the highest authority on the subject of optical activity and chemical composition, and his writings are always clear and accurate. In the original the chapter here translated is well known to chemists. Its appearance in English and in separate form will no doubt give it a wider circulation than it could secure as a part of an unwieldy and expensive book. The translation reads smoothly—something quite unusual in translations of chemical books from German into English. The translator has made certain notes and additions for the purpose of bringing the matter up to date.

I. R.

A SHORT HISTORY OF THE PROGRESS OF SCIENTIFIC CHEMISTRY IN OUR OWN TIMES. By WILLIAM A. TILDEN, D.Sc., Lond., D.Sc. Dub., F.R.S., Fellow of the University of London, Professor of Chemistry in the Royal College of Science. London: Longmans, Green & Co. 276 pp.

This is a well-written and interesting book, and one that will be helpful to students. It is, as the title indicates, a *short* history of the progress of chemistry. It consists of ten chapters, each of which deals with some important facts of the subject, and students of chemistry, even those who have a good knowledge of the history of their science, will find these chapters profitable reading. The titles are: I. Matter and Energy; II. The Chemical Elements: Their Distribution in Nature, and Recognition by the Chemist; III. Rectification and Standardization of Atomic Weights; IV. Numerical Relations among the Atomic Weights: Classification of the Elements; V. Origin and Development of the Ideas of Valency and the Linking of Atoms; VI. The Development of Synthetical Chemistry; VII. The Origin of Stereo-Chemistry—Constitutional Formulæ in Space; VIII. Electricity and Chemical Affinity; IX. Discoveries Relating to the Liquefaction of Gases; X. Summary and Conclusion.

In his preface the author says: "In the following pages I have endeavored to provide for the student such information as will enable him to understand clearly how the system of chemistry, as it now is, arose out of the previous order of

things; and for the general reader, who is not a systematic student, but who possesses a slight acquaintance with the elementary facts of the subject, a survey of the progress of chemistry as a branch of science during the period covered by the lives of those chemists, a few of whom only remain among us, who were young when Queen Victoria came to the throne."

And again he says: "Finally, I desire to point out that this does not profess to be a text-book giving a complete picture of the state of knowledge and of theory at the moment. Its object, as already stated, is to show by what principal roads we have arrived at the present position, in regard to questions of general and fundamental importance."

The book is cordially recommended to chemists, old and young. I. R.

THE KINETIC THEORY OF GASES. By O. E. MEYER. Translated from the second revised edition by ROBERT E. BAYNES. London and New York: Longmans, Green & Co. 1899. 472 pp.

The first edition of this book appeared in 1877 and was soon exhausted. The preparation of a revised edition was, however, postponed from time to time; and it was not published until a year ago. English readers are to be congratulated on the fact that the publishers secured the services as translator of Mr. Baynes, of Christ Church, Oxford. The translation is in every case accurate, fluent, and lucid, and the added notes are always valuable. The publishers have given us a book of convenient size and with excellent paper and type, so that it is a pleasure to read it.

The author divides his subject into two sections, relegating the more mathematical portions—the complicated formulæ and the manifold discussions—to "Mathematical Appendices" at the end of the book. These occupy over 100 pages of rather fine type and give, on the whole, a fair and ample discussion of the intricate questions which have excited so much interest among mathematicians and physicists. It is true that one does not feel, while reading these sections, the presence and strength of an original mind grappling with the difficulties, as one does in the two recent text-books on the kinetic theory of gases by Watson and by Burbury; but, in spite of this, the reader is given sufficient information to make all the later critical papers by Rayleigh, Boltzmann, and Planck interesting and intelligible.

The portion of the present book, however, which is the most valuable and which will be more widely read is included in the first 350 pages. This is divided into three parts: Molecular Motion and Its Energy; The Molecular Free Paths and the Phenomena Conditioned by Them; On the Direct Properties

of Molecules. There are ten chapters: Foundations of the Hypothesis; Pressure of Gases; Maxwell's Law; Ideal and Actual Gases; Molecular and Atomic Energy; Molecular Free Paths; Viscosity of Gases; Diffusion of Gases; Conduction of Heat; On the Direct Properties of Molecules. Each of these subjects is treated largely from an historical standpoint and in such a direct non-mathematical manner that it is delightful reading. The presentation of the various questions is of such a nature as to make them easily understood by all, even by those who may have had no previous knowledge of the subject. The mathematical formulae on the kinetic theory are deduced; the experimental determinations are described, full references being given; and discrepancies between theory and observation are critically discussed. One cannot speak too highly of this portion of the book. At times, naturally, exception may be taken to the use or definition of a word, or to the importance given certain hypotheses, but such criticisms do not deserve recording. The book is such a storehouse of observations, theoretical discussions, and experimental formulae, that it is invaluable for reference. The arrangement of the subject-matter is clear and logical, and the index—which we owe to Mr. Baynes--is full and accurate.

J. S. AMES.

THE COMPENDIOUS MANUAL OF QUALITATIVE CHEMICAL ANALYSIS OF C. W. ELIOT AND F. H. STORER, as revised by W. R. NICHOLS. Nineteenth edition. Newly revised by W. B. LINDSAY, Professor of General and Analytical Chemistry in Dickinson College, and F. H. STORER, Professor of Agricultural Chemistry in Harvard University. New York: D. Van Nostrand Co. 1899. 202 pp.

Among the multitude of works upon qualitative chemical analysis it is rare indeed to find a manual which has reached its nineteenth edition, and this fact alone would seem to render comment upon the merits of this work almost superfluous. It has proved itself to be, in many hands, a reliable guide alike for the general student, to whom it presents an excellent example of scientific methods of study, and for the professional student, who, within its scope, derives from it an excellent training in the manipulation, reasoning, and capacity for observation, which are essential for the successful analyst. The passage from this manual to those of wider scope is easy and natural for the student who has conscientiously followed its teachings.

The present edition has been rewritten and revised, although the changes are those of details, and do not alter the general character of the work. A notable change is that in the scheme for the separation of the members of the arsenic group, the fusion of the mixed sulphides with sodium car-

bonate and nitrate having been replaced by the separation by means of hydrochloric acid and the use of the generator. Some of the material has been rearranged, many subheadings have been introduced, and a great many additional and helpful comments and suggestions have been scattered through the text. Since much of the material of this character, new and old, has been printed in type smaller than that of the main body of the text, the size of the volume is not increased.

It is difficult to understand why, in the revision of this manual, the teaspoon has been retained as the standard of measure throughout the work. The graduated cylinder is as common a laboratory utensil as the beaker or test-tube, and the expenditure of time or thought in acquiring a concrete notion of the volume of 5 cc., which is stated in a foot-note to be the equivalent of the teaspoonful, is surely not serious. To find the use of a "teaspoonful of strong nitric acid" prescribed on one of its pages is disturbing in a work which has been prepared with such an evident and careful purpose to present the subject from a scientific standpoint.

H. P. TALBOT.

DESCRIPTIVE GENERAL CHEMISTRY. A TEXT-BOOK FOR SHORT COURSE. By S. E. TILLMAN, Professor of Chemistry, Mineralogy, and Geology, United States Military Academy. Second edition. New York: John Wiley & Sons. 8vo. 429 pp. $3.00, net.

In the preface to this new edition of the text-book in use at West Point, the author says that the time which can be allotted to the study of chemistry at that institution is very short, and the belief of the instructors has been "that the laboratory method alone, or mainly, in so short a course, could not be made of as much value to the pupils as the method making the acquisition of knowledge the essential feature; and that the best results could be reached through careful study of the proper text, well-conducted recitations accompanied by experimental and explanatory lectures. While accepting the general correctness of this conclusion, the author would add a small amount of well-selected laboratory practice."

Of course, if the time allotted to the study of chemistry is insufficient, the instructor must modify his instruction to fit the circumstances, but Professor Tillman, after speaking of the care given to the selection of the information in the book, continues: "The chemical knowledge most requisite to the average professional soldier differs but little from that essential to other educated men."

At first sight one might infer that in the author's opinion a similar system of instruction would be in place in colleges, instead of the prevailing laboratory system. Few teachers

would accept such a conclusion, nor indeed is it probable that the author means more than to suggest that the text-book found best for West Point would be equally valuable in colleges. This may be doubted. With time and facilities for laboratory work, text-books which constantly direct the attention of the student to experimental verification of the statements given will be preferred by most teachers.

For the students, for whose use it is primarily intended, the book is good. A more careful revision of the text of the new edition in the light of modern chemical knowledge would have been an improvement. For example, the statements that "ammonia is primarily organic in its origin," that "all hydrocarbons are primarily derived from the organic kingdom" cannot stand without ample qualification in view of what we know of the formation of nitrides and carbides at high temperatures, and of the action of water on these substances. E. R.

THE ARITHMETIC OF CHEMISTRY. Being a simple treatment of the subject of chemical calculations. By JOHN WADDELL, PH.D. New York: Macmillan Co. 136 pp. 90 cents.

This little book will be helpful to those college students who find difficulty in making chemical calculations, and will also be of service to teachers, showing them how to explain a subject, like the measurement of gases, in a clear way. Several useful tables and a number of problems taken from English and American university examination papers add to the value of the book. E. R.

EXPERIMENTELLE EINFÜHRUNG IN DIE UNORGANISCHE CHEMIE. Von HEINRICH BILTZ. Leipzig: Veit & Co. 1900.

In this little laboratory manual Professor Biltz has added to the usual simple reactions of inorganic compounds a number which are based on the current theory of aqueous solutions. The book is clear and modern. E. R.

QUALITATIVE ANALYSE UNORGANISCHER SUBSTANZEN. Von HEINRICH BILTZ. Leipzig: Veit & Co. 1900.

This, too, is a small laboratory manual. The analytical methods recommended are the best and newest. E. R.

LES PARFUMS ARTIFICIELS. Par EUGÈNE CHARABOT, Chimiste Industriel, Professeur d'Analyse chimique a l'Institut Commercial de Paris. Paris: J. B. Baillièr et Fils. 1900. 296 pp.

There have been rapid advances in the field of the chemistry of perfumes during the past few years, and it will therefore be of interest to chemists to read this book, which gives a brief and clear account of the principal discoveries of importance in the field. The titles of the chapters are: I. Nitro

Compounds; II. Alcohols and Ethers; III. Phenols and Ethers of Phenols; IV. Aldehydes; V. Ketones; VI. Olides. The many varieties of artificial musk are treated of in Chapter I. There appears to be a great demand for this perfume, though why, it would be hard to say. There are to be sure some odors to which it is to be preferred, but not many.

The author says: "The synthetical perfumes which, from the point of view of their applications, are most interesting are *terpineol*, *vanilline*, *piperonal* or *heliotropine*, *ionone* or *artificial violet*, and *artificial musk*." Terpineol is made by the dehydration of terpenes. It was put upon the market in 1889 and is now very extensively used for perfuming soaps. It also enters into the composition of a large number of bouquets, especially syringa and lilac. The story of ionone or artificial violet is the most interesting in the book, from the scientific as well as from the commercial point of view. According to the author: "The discovery of ionone, which is now extensively employed, has not worked any injury to the cultivation of the violet in the department of the Maritime Alps. In fact, this cultivation has extended since 1893 without leading to a lowering of the price of the flower."

It is interesting to note that piperonal or heliotropine, which in 1879 cost 3790 francs a kilogram, cost only 37.5 francs a kilogram in 1899. I. R.